

The UV-Spectra of Substituted Polyene Hydrocarbons
and the Ferro-Antiferromagnetic Transition
Temperatures in Compounds
of Fe, Co, and Ni

By
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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
February, 1962

ACKNOWLEDGEMENT

The author is greatly indebted to his Advisory Committee for assistance and guidance in the completion of this research. Special thanks is due to Dr. E. E. Muschlitz, Jr., who served as chairman of his committee and made valuable suggestions in the preparation of the manuscript. The author also wishes to express his sincere gratitude to Dr. D. W. Smith, who suggested an improved treatment of Part I and made many helpful suggestions, and to Dr. T. A. Scott who has reviewed Part II with great care.

The late Dr. J. E. Hawkins deserves special acknowledgement. He guided and inspired the author, and also served as his original committee chairman.

The author owes a debt of gratitude to his wife who typed the rough draft and helped him in many other ways.

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PART I

THE UV-SPECTRA OF SUBSTITUTED POLYENE HYDROCARBONS

CHAPTER I

INTRODUCTION

It is quite often of interest for chemists to be able to estimate the absorption maxima λ_0 for the ultraviolet (UV) spectra in the course of resolving the structure of conjugated hydrocarbons.

It has been known for a long time that substituted alkyl groups on these compounds (both aromatic and aliphatic) have a bathochromic effect, or a shift towards a longer wave length in the ultraviolet spectra. Mulliken¹ interpreted, for example, the bathochromic effect of the methyl group on the benzene ring in terms of hyperconjugation. There also exists the well known "Woodward"² method which predicts absorption maxima for aromatic compounds.

Mulliken's treatment is, however, too cumbersome to employ and Woodward's method is purely empirical and not always reliable. It is desirable, therefore, to have a scheme for predicting for alkyl substituted polyenes which is simple to use, would have some theoretical basis, and would produce reasonably good results.

In the attempt to find an existing scheme for doing this, the literature was examined rather extensively. Numerous methods and examples were found for cata-condensed aromatic systems such as benzene, naphthalene, and anthracene, etc., and for polyenes such as butadiene, and hexatriene, etc.

The MO-LCAO³ (molecular orbital by linear combination of atomic orbitals) method as well as the FEMO^{4,5,6} (free electron molecular orbital) method were used widely for those compounds mentioned above. Although these methods seem to be very successful and satisfactory in treating pi-electron systems, none of these methods are very suitable for the alkyl substituted complex systems.

The particular interests in this laboratory have been the investigation of physical properties of terpene hydrocarbons.⁷ These are a class of compounds whose molecular formulas are $C_{10}H_{16}$, in which conjugated double bonds as well as localized sigma bonds are found. For these and other systems containing more than two or three atoms, it is extremely difficult to set up wave functions and solve secular equations in a rigorous manner. To overcome this type of difficulty and facilitate the calculations, Hückel,⁸ Wheland,⁹ and Pauling and Wheland¹⁰ have independently developed very valuable approximate methods. The perturbation method,¹¹ however, developed by Dewar and Longuet-Higgins, was found rather convenient and very useful in treating polyene hydrocarbons.

The purpose of this research was to improve the existing approximation methods by introducing the effect of a substituent group or groups on the parent compound in terms of exchange integrals β as well as incorporating the idea of hyperconjugation. The present investigation, therefore, differs from others in the following three points:

1. No additional parameters are introduced; i.e., the Hückel approximation is retained.
2. Hyperconjugation effects are taken into account in the calculation.

3. Different β values are used for different compounds depending upon the effective number of substituents.

As will be seen in the following chapters, this simple approximation proves to be an excellent method to estimate absorption maxima in the ultraviolet spectra for the polyene hydrocarbons.

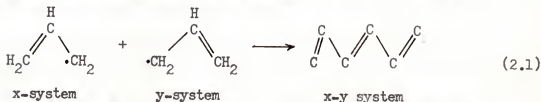
CHAPTER II

THEORY

The Perturbation Method of Dewar and Longuet-Higgins

The perturbation theory developed by Dewar and Longuet-Higgins¹¹ essentially consists of building up molecules from fragments. For its detailed account, the original paper by the same authors¹¹ or pages 83-90 of Quantum Chemistry by Daudel, Lefebvre, and Moser¹² should be consulted.

Consider, for example, a hexatriene molecule. It may be considered as being built from two allyl radicals, x and y:



For the x-system, let φ_1 , φ_2 and φ_3 be the properly normalized atomic orbitals associated with carbon atoms 1, 2, and 3. The MO's will have the form,

$$\psi_x = C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3. \quad (2.2)$$

Assuming ψ_x is a solution of the equation

$$H_x \psi_x = E_x \psi_x, \quad (2.3)$$

or

$$(H_x - E_x) \psi_x = 0,$$

where

$$H_x = T + V_x, \quad (2.4)$$

and substitution of equation (2.2) into (2.3) leads to

$$C_1(H_x - E_x)\varphi_1 + C_2(H_x - E_x)\varphi_2 + C_3(H_x - E_x)\varphi_3 = 0. \quad (2.5)$$

Multiplying equation (2.5) by φ_1 and integration over all space gives

$$C_1 \int \varphi_1(H_x - E_x)\varphi_1 dv + C_2 \int \varphi_1(H_x - E_x)\varphi_2 dv + C_3 \int \varphi_1(H_x - E_x)\varphi_3 dv = 0 \quad (2.6)$$

By the same procedure, the following equations are obtained:

$$C_1 \int \varphi_2(H_x - E_x)\varphi_1 dv + C_2 \int \varphi_2(H_x - E_x)\varphi_2 dv + C_3 \int \varphi_2(H_x - E_x)\varphi_3 dv = 0, \quad (2.7)$$

$$C_1 \int \varphi_3(H_x - E_x)\varphi_1 dv + C_2 \int \varphi_3(H_x - E_x)\varphi_2 dv + C_3 \int \varphi_3(H_x - E_x)\varphi_3 dv = 0. \quad (2.8)$$

To simplify the notations, the Coulomb integral α , the exchange integral β , and overlap integral S , are defined as follows:

$$\begin{aligned} \alpha_{ii} &= \int \varphi_i H_x \varphi_i dv, \\ \beta_{ij} &= \int \varphi_i H_x \varphi_j dv, \\ S_{ij} &= \int \varphi_i \varphi_j dv. \end{aligned} \quad (2.9)$$

Since normalized AO's have been used, one may write

$$E_x = \int \varphi_i E_x \varphi_i dv. \quad (2.10)$$

Using these definitions, equations (2.6), (2.7), and (2.8) become:

$$\begin{aligned} C_1(\alpha_{11} - E_x) + C_2(\beta_{12} - E_x S_{12}) + C_3(\beta_{13} - E_x S_{13}) &= 0, \\ C_1(\beta_{21} - E_x S_{21}) + C_2(\alpha_{22} - E_x) + C_3(\beta_{23} - E_x S_{23}) &= 0, \\ C_1(\beta_{31} - E_x S_{31}) + C_2(\beta_{32} - E_x S_{32}) + C_3(\alpha_{33} - E_x) &= 0. \end{aligned} \quad (2.11)$$

These simultaneous equations have non-trivial solutions if and only if the determinant of the coefficients of the C 's is zero, i.e.,

$$\begin{vmatrix} \alpha_{11} - E_x & \beta_{12} - E_x S_{12} & \beta_{13} - E_x S_{13} \\ \beta_{21} - E_x S_{21} & \alpha_{22} - E_x & \beta_{23} - E_x S_{23} \\ \beta_{31} - E_x S_{31} & \beta_{32} - E_x S_{32} & \alpha_{33} - E_x \end{vmatrix} = 0. \quad (2.12)$$

In the Hückel approximation, it is assumed that

$$\alpha_{11} = \alpha_{22} = \alpha_{33} = \alpha,$$

$$\beta_{12} = \beta_{23} = \beta_{32} = \beta_{21} = \beta,$$

$$\beta_{13} = \beta_{31} = 0,$$

$$S_{12} = S_{21} = S_{13} = S_{31} = S_{23} = S_{32} = 0. \quad (2.13)$$

When the Hückel approximation is introduced into equation (2.12), it reduces to:

$$\begin{vmatrix} \alpha - E_x & \beta & 0 \\ \beta & \alpha - E_x & \beta \\ 0 & \beta & \alpha - E_x \end{vmatrix} = 0. \quad (2.14)$$

Dividing every term in the determinant by β and letting

$$\frac{\alpha - E_x}{\beta} = m_x, \quad (2.15)$$

one obtains

$$\begin{vmatrix} m_x & 1 & 0 \\ 1 & m_x & 1 \\ 0 & 1 & m_x \end{vmatrix} = 0. \quad (2.16)$$

Solving equation (2.16) for m_x , the following three roots are obtained: $m_x = 0$, and $\pm \sqrt{2}$.

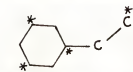
From equation (2.15),

$$E_x = \alpha \pm m_x \beta. \quad (2.17)$$

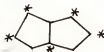
In equation (2.17), the orbital is said to be "bonding," "antibonding," and "non-bonding" according to whether m_x is positive, negative, or zero.

At this point it is necessary to introduce the terminology of Coulson and Rushbrooke.¹³ These authors classified compounds into "alternant," and "non-alternant" systems according to whether

or not the carbon atoms in the compound can be separated into two sets, where each atom in one set (the "starred" set) can have only atoms from the other set (the "unstarred" set) as neighbors. This is illustrated in the diagrams below.



alternant system



non-alternant system

For alternant systems, the orbitals occur in pairs in the sense that for every orbital j with energy $\alpha + m_{xj}\beta$, there is another orbital with energy $\alpha - m_{xj}\beta$. This relation may be seen from the result just derived for the system x for the bonding and antibonding orbitals. This relation is known as the pairing theorem.¹³

In the Hückel approximation, the number of orbitals becomes equal to the number of carbon atoms and, if the molecule is an odd-alternant system, there will be one non-bonding orbital with $m_x = 0$ and $E = \alpha$. In the ground state it is the highest occupied orbital and is half filled.

Repeating the same procedure for the y -system and x - y system, the following energies are obtained:

<u>x-system</u>	<u>y-system</u>	<u>x-y system</u>
.....	$\alpha - m_{xy1}\beta$
.....	$\alpha - m_{xy2}\beta$
$\alpha - m_x\beta$	$\alpha - m_y\beta$	$\alpha - m_{xy3}\beta$
α	α

<u>x-system</u>	<u>y-system</u>	<u>x-y system</u>
$\alpha + m_x/\beta$	$\alpha + m_y/\beta$	$\alpha + m_{xy}3/\beta$
.....	$\alpha + m_{xy}2/\beta$
.....	$\alpha + m_{xy}1/\beta$

The Dewar and Longuet-Higgins perturbation method provides a simple and convenient scheme for finding the highest occupied and lowest unoccupied orbitals in the x-y system.

Let H_x and H_y be the one electron Hamiltonian for the MO in the x and y fragments and ψ_{xi} and ψ_{yj} be the approximate solutions of the equations

$$H_x \psi_{xi} = E_{xi} \psi_{xi}, \quad (2.18)$$

$$H_y \psi_{yj} = E_{yj} \psi_{yj}, \quad (2.19)$$

where

$$H_x = T + V_x, \quad (2.20)$$

$$H_y = T + V_y, \quad (2.21)$$

in which T is a kinetic energy operator, V_x and V_y are potential energy operators for the x and y-systems.

Let the total Hamiltonian for the system x-y be

$$H = T + V_x + V_y. \quad (2.22)$$

Then for the case that one of the E_{xi} 's is equal to one of the E_{yj} 's, certain orbitals of the x-y system may be approximated by the linear combination

$$\psi = a\psi_x + b\psi_y. \quad (2.23)$$

The problem of obtaining the energy associated with equation (2.23) then becomes the problem of resolving the following determinant:

$$\begin{vmatrix} H_{xx} - E_{xy} & H_{xy} \\ H_{yx} & H_{yy} - E_{xy} \end{vmatrix} = 0, \quad (2.24)$$

where

$$\begin{aligned} H_{xx} &= \int \psi_x H \psi_x dv, \quad H_{yy} = \int \psi_y H \psi_y dv, \\ H_{xy} &= \int \psi_x H \psi_y dv, \quad H_{yx} = \int \psi_y H \psi_x dv. \end{aligned} \quad (2.25)$$

When these integrals are evaluated for the two non-bonding orbitals of energy $E = \alpha$ of the odd alternant hydrocarbons x and y , the following values are obtained:

$$\begin{aligned} H_{xx} &= \int \psi_x (T + V_x + V_y) \psi_x dv \\ &= \int \psi_x (T + V_x) \psi_x dv + \int \psi_x V_y \psi_x dv \\ &= \alpha, \end{aligned} \quad (2.26)$$

where the second integral term $\int \psi_x V_y \psi_x dv$ has been neglected because V_y is not important in the region of ψ_x . Similarly,

$$H_{yy} = \alpha. \quad (2.27)$$

Now ψ_x and ψ_y may be expanded in terms of atomic orbitals ϕ_k and $\phi_{k'}$ in the following way,

$$\psi_x = \sum_k C_{kx} \phi_k \quad (2.28)$$

$$\psi_y = \sum_{k'} C_{ky'} \phi_{k'} \quad (2.29)$$

where C_{kx} and $C_{ky'}$ are expansion coefficients for the x and y -system, respectively. Consequently,

$$\begin{aligned} H_{xy} &= \int \psi_x H \psi_y dv \\ &= \sum_k \sum_{k'} C_{kx} C_{ky'} \int \phi_k H \phi_{k'} dv. \end{aligned} \quad (2.30)$$

In equation (2.30), since indices k are all different from k' , there are no α terms, and the only non-vanishing terms in the Hückel scheme are the terms $\int \phi_k H \phi_{k'} dv = \beta$, with atom k adjacent to atom k' . In the present example only one such term arises, corresponding to the bond joining x and y . Therefore, equation (2.30) can be written as:

$$H_{xy} = C_x C_y \beta. \quad (2.31)$$

likewise,

$$H_{yx} = C_x C_y \beta = H_{xy}. \quad (2.32)$$

In equation (2.32), $H_{yx} = H_{xy}$ because the Hamiltonian is a hermitian operator and the wave functions are real.

Substituting all these values into equation (2.24) and solving, one obtains by the perturbation method

$$(\alpha - E_{xy})^2 = (C_x C_y)^2 \beta^2,$$

and therefore

$$E_{xy} = \alpha \pm C_x C_y \beta. \quad (2.33)$$

It is interesting to compare equation (2.33) with the corresponding energy expression (2.34) as obtained by solving the full secular equation for hexatriene:

$$\begin{aligned} E &= \alpha \pm 2\beta \cos(3\pi/7) \\ &= \alpha \pm 0.48\beta. \end{aligned} \quad (2.34)$$

Since the perturbation method gives the coefficients $C_x = C_y = 1/\sqrt{2}$ for hexatriene, equation (2.33) becomes

$$E = \alpha \pm 0.5\beta.$$

Thus, it may be seen the perturbation method gives approximately the same value as obtained by the rigorous solution.

According to the perturbation method, the energy separation E between the highest occupied and the lowest unoccupied levels may be given by

$$\Delta E_{xy} = 2C_x C_y \beta. \quad (2.35)$$

This energy separation corresponds to the first electronic transition and it can be given by the following formula, in general:

$$\Delta E = h\nu_0 = 2 \sum C_x C_y \beta, \quad (2.36)$$

where ν_0 is the average frequency of the absorption band.

In terms of wave length λ .,

$$\lambda. = c/\nu. = hc/(2 \sum C_x C_y \beta), \quad (2.37)$$

where c is the velocity of the light.

If the coefficients C_x and C_y , and the exchange integral β are known, $\lambda.$ can be evaluated from equation (2.37), giving a very convenient method of calculating the first excitation energy of the alternant system.

Extension of the Perturbation Method for Methyl Substituted Polyenes

Although the perturbation method of Dewar and Longuet-Higgins described in the preceding section is applicable in principle to alkyl substituted polyenes, it requires a considerable amount of labor and skill. Therefore, it was decided to develop a simpler method by extending Dewar's perturbation treatment.

It will be assumed that the three hydrogen atoms on a methyl group may be considered as a pseudo atom (the idea of a pseudo atom was conceived by Mulliken¹), and that the difference in electronegativity between the carbon and the pseudo atom can be neglected; and that, whenever methyl groups are substituted in the conjugated system, the three bonds in the methyl group may be regarded as two sigma bonds and one pi-bond where the pi-bond is considered to take part in the conjugated system.

In the ordinary LCAO treatment, β is regarded as a parameter to be determined empirically. In the case of polyenes, it is to vary β with the length of the chain or number of pi-electron centers in the compound in order to obtain agreement with the ultraviolet absorption spectra. In the present research it was

noted that β must be varied with the number of substituents in order to fit the spectra.

To this end, 1,3-butadiene was chosen as the parent compound and β was evaluated from the observed absorption maximum in the ultraviolet spectrum by following equation given by the LCAO¹⁴ method:

$$\beta = \frac{hc}{4 \lambda \sin \frac{\pi}{2(2N+1)}} \quad (2.38)$$

where N is equal to the number of double bonds. This basic β was then compared with the one obtained by equation (2.37) for a mono-methyl substituted 1,3-butadiene or 1,3-pentadiene and the difference in β was ascribed to a methyl group and termed as $\beta\text{-CH}_3$.

In examining a number of examples, it was found that the absorption maximum could be predicted for compounds with one or more methyl substituents by using the following formula:

$$\beta = \beta_{\text{basic}} + n \times \beta\text{-CH}_3, \quad (2.39)$$

where n is the effective number of methyl substituents.

Not all of the substituents are effective because some do not always behave as perturbing sources. The effective number n can be evaluated by breaking up a molecule into two odd alternant systems as described previously, calculating coefficients in the highest occupied orbital, and counting only the number of substituents which have non-zero coefficients.

CHAPTER III

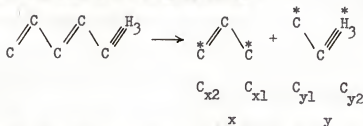
CALCULATIONS

As already described in the previous chapter, β is evaluated by equation (2.38) taking $\lambda_0 = 209 \text{ m}\mu^*$ as follows:

$$\begin{aligned}\beta &= \frac{hc}{4 \lambda_0 \sin \frac{\pi}{2(2N+1)}} \\ &= \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{4 \times 2.09 \times 10^{-5} \times \sin \frac{180}{10}} \\ &= 7.65 \times 10^{-12} \text{ ergs.}\end{aligned}\tag{3.1}$$

Now in order to evaluate the perturbation effect of the methyl group on the parent compound, 1,3-butadiene, a cis-1,3-pentadiene molecule whose observed absorption maximum is $217 \text{ m}\mu$, is chosen as a reference substance.

This molecule is then broken up into two odd radicals as shown and labelled x and y-systems.



In calculating coefficients C_{x1} and C_{y1} , the normalization condition and "coefficient theorem"¹⁵ are used. As applied to

* References to the experimental λ_0 values may be found below Table 1.

the non-bonding molecular orbital in an odd alternant hydrocarbon the coefficient theorem states that the sum of coefficients of the atomic orbitals for the starred atoms adjacent to any unstarred atom is always zero. That is, in cis-1,3-pentadiene,

$$C_{x1}^2 + C_{x2}^2 = 1, C_{x1} + C_{x2} = 0.$$

Likewise,

$$C_{y1}^2 + C_{y2}^2 = 1, C_{y1} + C_{y2} = 0.$$

Therefore,

$$C_{x1} = C_{y1} = 1/\sqrt{2}.$$

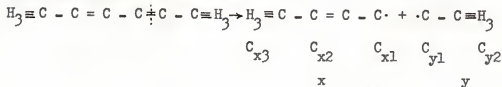
Using equation (2.37), β which is required for agreement with the observed $\lambda = 217 \text{ m}\mu$, is evaluated as follows:

$$\beta = \frac{hc}{2C_{x1}C_{y1}\lambda} = \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/2 \times 1/2 \times 2.17 \times 10^{-5}} = 9.12 \times 10^{-12} \text{ ergs.} \quad (3.2)$$

The difference in β values for 1,3-butadiene and 1,3-pentadiene is considered to be the perturbation effect of the methyl group and is assigned the value $\beta_{-\text{CH}_3} = 1.47 \times 10^{-12} \text{ ergs}$. Equation (2.39) can be rewritten, upon substitution of numerical values of β_{basic} and $\beta_{-\text{CH}_3}$, as

$$\beta = (7.65 + n \times 1.47) \times 10^{-12}. \quad (3.3)$$

2.4-Hexadiene. This compound is considered to consist of the following x and y-systems:



From the normalization condition and the coefficient theorem, the coefficients C_{x1} and C_{y1} are obtained as follows:

$$C_{x1} = 1/\sqrt{3}, C_{y1} = 1/\sqrt{2}.$$

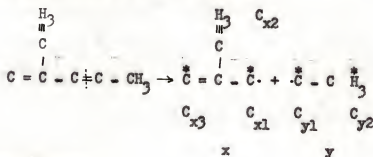
In this case, both methyl groups have non-zero coefficients.

Therefore, β is taken to be 10.59×10^{-12} ergs.

Therefore,

$$\lambda = \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/\sqrt{3} \times 1/\sqrt{2} \times 10.59 \times 10^{-12}} \\ = 229 \text{ m}\mu.$$

2-Methyl-1,3-pentadiene. This molecule is decomposed into the x and y-radicals as shown below:



In the x-system,

$$C_{x1}^2 + C_{x2}^2 + C_{x3}^2 = 1, \text{ and}$$

$$C_{x1} + C_{x2} + C_{x3} = 0.$$

Since

$$C_{x2} = 0, C_{x1} = 1/\sqrt{2}.$$

In the y-system,

$$C_{y1}^2 + C_{y2}^2 = 1,$$

$$C_{y1} + C_{y2} = 0.$$

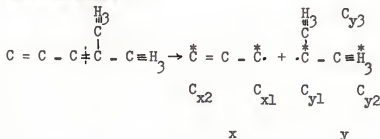
Therefore,

$$C_{y1} = 1/\sqrt{2}.$$

Although this compound has two substituted methyl groups, the methyl group on the x-system has zero coefficient. It thus has no effect on the system. Therefore, β is taken to be equal to $(7.65 + 1.47) \times 10^{-12}$ or 9.12×10^{-12} ergs, and

$$\lambda = \frac{hc}{2 C_{x1} C_{y1} \beta} = \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/\sqrt{2} \times 1/\sqrt{2} \times 9.12 \times 10^{-12}} = 217 \text{ m}\mu.$$

4-Methyl-1,3-pentadiene. Breaking up this molecule into the x and y-systems,



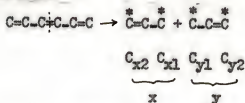
the coefficients are found to be

$$C_{x1} = 1/\sqrt{2}, C_{y1} = 1/\sqrt{3}.$$

Here again both methyl groups have non-zero coefficients and so taking $\beta = 10.59 \times 10^{-12}$ ergs,

$$\lambda = \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/\sqrt{2} \times 1/\sqrt{3} \times 10.59 \times 10^{-12}} = 229 \text{ m}\mu.$$

1,3,5-Hexatriene.



This compound is broken into the x and y-fragments above and

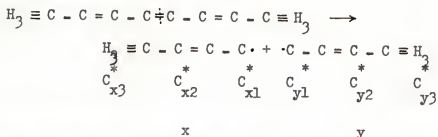
the same procedure gives

$$C_{x1} = 1/\sqrt{3}, C_{y1} = 1/\sqrt{2}.$$

Since the substituted methyl group has non-zero coefficient, the value of 9.12×10^{-12} ergs is taken for β . Therefore,

$$\begin{aligned}\lambda_0 &= \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/\sqrt{3} \times 1/\sqrt{2} \times 9.12 \times 10^{-12}} \\ &= 266 \text{ m}\mu.\end{aligned}$$

2,4,6-Octatriene. This molecule is decomposed into two 2-butene radicals,



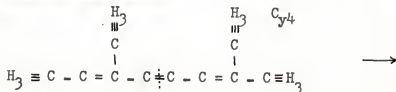
The application of the coefficient theorem and normalization condition gives

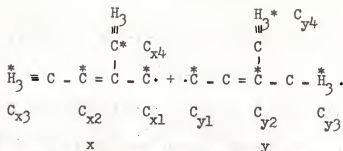
$$C_{x1} = C_{y1} = 1/\sqrt{3}.$$

Since both methyl groups have non-zero coefficients, the $\beta = 10.59 \times 10^{-12}$ ergs is taken for the calculation. Therefore,

$$\begin{aligned}\lambda_0 &= \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/\sqrt{3} \times 1/\sqrt{3} \times 10.59 \times 10^{-12}} \\ &= 280 \text{ m}\mu.\end{aligned}$$

Allo-ocimene. Allo-ocimene is decomposed into two isoprene units as shown below:





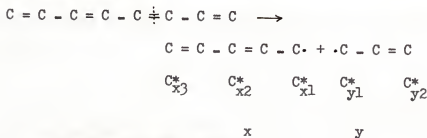
Using both the coefficient theorem and normalization condition, one obtains

$$C_{x1} = 1/\sqrt{3}, C_{y1} = 1/2.$$

Of four methyl groups only three have non-zero coefficients and therefore β is taken to be 12.06×10^{-12} ergs.

$$\begin{aligned}
 \lambda_0 &= \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/\sqrt{3} \times 1/2 \times 12.06 \times 10^{-12}} \\
 &= 284 \text{ m}\mu.
 \end{aligned}$$

Octatetraene. Octatetraene is broken into the x and y-radicals as shown below:



The same procedure gives

$$C_{x1} = 1/\sqrt{3}, C_{y1} = 1/\sqrt{2}.$$

Therefore,

$$\begin{aligned}
 \lambda_0 &= \frac{6.6 \times 10^{-27} \times 3 \times 10^{10}}{2 \times 1/\sqrt{3} \times 1/\sqrt{2} \times 7.65 \times 10^{-12}} \\
 &= 317 \text{ m}\mu.
 \end{aligned}$$

CHAPTER IV

RESULTS AND DISCUSSION

For convenience the calculated and observed results for the ultraviolet absorption spectra for the series of compounds investigated are tabulated in Table 1. It is seen that the agreement is excellent between the observed and calculated results. The deviations range from one $m\mu$ for 1,3,5-hexatriene to seventeen $m\mu$ for 2,4,6-octatriene. The magnitude of the deviations observed in this study is small in comparison with other investigations. Platt,¹⁶ for example, using the LCAO methods, observed a deviation of -5 $m\mu$ for 1,3,5-hexatriene, -29 $m\mu$ for ethylene, and -36 $m\mu$ for 1,3-butadiene.


The principal features of the present research are the variation of β as a function of the effective number of substituents instead of the number of pi-electron centers, and the use of an average β value for each calculation. The latter part of this statement implies that no distinctions are made between β values for different bonding in the same molecule. This may be contrasted, for example, with the treatment of toluene  by Coulson and Crawford,¹⁷ In their calculations, they used $\beta_{12} = 11.9 \times 10^{-12}$ ergs, $\beta_{23} = 3.13 \times 10^{-12}$ ergs and $\beta_{cc} = 4.76 \times 10^{-12}$ ergs. It is of interest to note that the β used for short polyenes by Platt¹⁶ is close to the basic β obtained

Table 1
Observed and Calculated UV-Absorption Maxima for
Polyene Hydrocarbons

Nomenclature	(m μ)		(m μ) Deviation	(ergs) $\beta \times 10^{12}$
	obs.	calc.		
1,3-butadiene	209 ^a	standard		7.65
1,3-pentadiene	217 ^b	standard		10.59
2,4-hexadiene	227 ^c	229	+ 2	10.59
2-methyl-1,3-pentadiene	220 ^d	217	- 3	9.12
4-methyl-1,3-pentadiene	223 ^e	229	+ 6	10.59
1,3,5-hexatriene	260 ^f	259	- 1	7.65
2-methyl-1,3,5-hexatriene	267 ^g	259	- 8	7.65
2-methyl-1,3,5-heptatriene	261 ^h	266	+ 5	9.12
2,4,6-octatriene	263 ⁱ	280	+17	10.59
allo-ocimene	280 ^j	284	+ 4	12.06
octatetraene	302 ^k	317	+15	7.65

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- a American Petroleum Institute Project 44, Serial Number 65
b ibid., Serial Number 46
c H. Booker, L. K. Evans, A. E. Gillam, J. Chem. Soc., 1453 (1940)
d American Petroleum Institute Project 44, Serial Number 66
e ibid., Serial Number 68
f M. Kovner, Acta Physicochim., U.R.S.S., 19, 385 (1944)
g E. A. Braude and C. J. Timmons, J. Chem. Soc., 2000 (1950)
h ibid., 2007 (1950)
i E. R. Blout and M. Fields, J. Am. Chem. Soc., 70, 189 (1948)

from 1,3-butadiene in this work.

The present method is superior to other treatments in simplicity, and convenience. The semi-empirical nature of the method is dictated by the complexity of the molecules considered. It would be desirable, in future work, to determine the effect on β of a substituent methyl group by direct calculation in order to give a sounder theoretical basis for the present work. The method might also be improved and extended by considering different β values for different types of bonding in a given molecule.

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- j R. D. Walker, Jr. and J. E. Hawkins, J. Am. Chem. Soc., **74**, 4209 (1952)
- k H. Kuhn, J. Chem. Phys., **17**, 1198 (1949)

CHAPTER V

SUMMARY

In the theoretical calculation of the absorption maxima of ultraviolet spectra for alkyl-substituted polyene hydrocarbons, the Dewar and Longuet-Higgins' perturbation method was extended by incorporating the idea of hyperconjugation and also by varying β as a function of the effective number of substituents. This simple scheme has proved to be a very effective and powerful method in predicting absorption maxima of ultraviolet spectra for alkyl substituted polyene hydrocarbons.

PART II

THE FERRO-ANTIFERROMAGNETIC TRANSITION TEMPERATURES

IN COMPOUNDS OF Fe, Co, AND Ni

CHAPTER VI

INTRODUCTION

In their heat capacity measurements at low temperatures, Stout, et al.,¹⁸ observed specific heat anomalies for MnF_2 , FeF_2 , and CoF_2 , etc. They ascribed these anomalies to the magnetic ordering of atoms in crystalline lattices.

In a theoretical treatment of this antiferro-ferromagnetic transition, for example, Néel¹⁹ considered a physical model of magnetic ions of two interpenetrating sublattices having opposite alignments of moments in which the neighbors of the ions of one sublattices belong to the other sublattices. The magnetic property of such an arrangement is called "antiferromagnetism." On the other hand, Van Vleck²⁰ developed an approximate treatment for ferromagnetism similar to the Weiss molecular field approximation.

Much earlier than these theoretical studies, Ising²¹ formulated a model, which is essentially based on the view that ferromagnetism is due to an interaction between the spins of certain atoms making up a crystal.

Yomosa²² developed a statistical method based on the Ising model in connection with the Bethe-Peierls²³ method and applied it to the spin systems of FeCl_2 . The purpose of this investigation was to extend his work to the study of the relationship of the

Nèel, or Curie temperature and the spin coupling constants of compounds having different crystalline structures such as MnCl_2 , FeCl_2 , and CoCl_2 having close-packed hexagonal arrangement and CoF_2 having the rutile-type structure as well as establishing a definite existence of second transition temperature in the former compounds. The observed results were compared to the results expected from theoretical considerations.

CHAPTER VII

THEORY

The anhydrous difluorides of Mn, Fe, and Ni all have the rutile-type crystal structure,²⁴ while dichlorides of these elements have close-packed hexagonal crystalline structure.^{18,22} According to Stout and Adams,²⁵ MnF_2 exhibits a maximum in the powder magnetic susceptibility and also, at about the same temperature, a region of anomalously high heat capacity which is an indication of a cooperative phenomenon. These authors also observed that one of the principal axes of magnetic susceptibility lies along the c-axis of the crystal. Van Vleck²⁰ in his theory of antiferro-magnetism also predicted that the magnetic susceptibility of an antiferromagnetic substance below Néel temperature should decrease with temperature in the direction of the c-axis. The spin of two sublattices are aligned parallel and antiparallel along the c-axis and the magnetic susceptibility along this axis should approach zero at 0°K, while the magnetic susceptibility perpendicular to the c-axis would remain constant below the Curie temperature.

This alignment of the spin has been further confirmed by neutron diffraction measurements by Erickson and Shull.²⁶ They not only confirmed that the c-axis is the direction along which alignment occurs, but also that the spins in the nearest neighbor

columns in the direction of the c-axis are all aligned parallel to one another. Therefore, each column is surrounded by four others which have spin antiparallel to it.

The ordered magnetic structure consistent with the magnetic susceptibility and neutron diffraction data can be drawn for FeF_2 as shown in Figure 1.

Kanamori²⁷ in his theoretical investigation of the antiferromagnetic substance, FeCl_2 , concluded that, if the spins are unable to deviate from the c-axis, the Ising model is well applicable to the spin systems of FeCl_2 . From his results, the lowest lying orbital state of Fe^{++} ion is a doublet and their components of the orbital angular momentum have matrices

$$L_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad L_x = L_y = 0. \quad (7.1)$$

In reference to Figure 1, each crystal lattice point is associated with a spin coordinate α . All the particles are assumed to be localized at their respective crystal lattice points and to be independent of spin configuration. Considering α as a scalar quantity, the value $\alpha = +1$ is assigned to a spin state with the spin in some preassigned direction, say "up," such as shown by the lattice points 0, 1, ..., 8, and $\alpha = -1$ to a spin in the opposite direction, or "down," such as in lattice sites 9, 11, ..., 16. Before developing a partition function for the FeF_2 system, it seems to be proper to mention two fundamental postulates²⁸ underlying the "Ising" model.

First postulate: Only particles on nearest neighbor lattice points interact. According to this postulate, the interaction

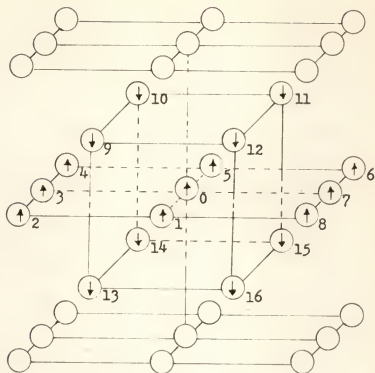


Figure 1. The spin arrangement in FeF₂. Only positive ferrous ions are shown in the diagram.

energy between two particles at i -th and j -th lattice points and having spins σ_i and σ_j , respectively, is then

$$E_{ij} = \begin{cases} \pm J \sigma_i \sigma_j & \text{if } i \text{ and } j \text{ are nearest neighbors,} \\ 0 & \text{otherwise.} \end{cases} \quad (7.2)$$

The energy is $+J$ if the nearest neighbors have the same spin and is $-J$ if they have opposite spins. The constant J appearing as a parameter is a measure of the strength of this coupling and J is positive for a ferromagnetic and negative for an antiferromagnetic system.

Second postulate: The particle can interact with an external magnetic field. The interaction energy of the j -th particle of a magnetic moment μ , with the external field strength, H , is then

$$E_H = -\mu H \sigma_j. \quad (7.3)$$

On these two postulates, we can develop a partition function for the spin systems of FeF_2 .

CHAPTER VIII

CALCULATIONS

FeF_2

As was pointed out in the previous section, the magnetic ordered state of positive Fe^{++} ion in the FeF_2 crystal may be imagined as shown in Figure 1. If the layer occupied by lattice points 0, 1, 2, ..., 8 is labelled A and either the layer occupied by lattice points 9, 10, ..., 12 or 13, 14, ..., 16 is labelled B, and if all the spins of the particles in the A layer are considered up and those in the B layers considered down as indicated by the arrow heads in Figure 1, and if the 0-th atom is chosen as a central atom then the ferromagnetic interactions between the electrons of the atoms in the same layer and the antiferromagnetic interactions between those in the different layer can be considered in the following manner. In applying the "Ising model" to the (1 + 16) particle cluster system, a certain approximation had to be made. In the layer A, for example, the particles 2, 4, 6, and 8 should be omitted in principle from our consideration if we should adhere to the first postulate of the "Ising model," since they are second nearest neighbors to the central atom.

Since the ratio of the second to the closest neighbor from the central atom is only 1.12 in FeF_2 , it seemed advisable to include the second nearest in our calculation. As an approximation, therefore, it is assumed that each lattice point 1, 2, 3, ..., 9

occupies the apex of a regular octagon instead of a regular tetrahedron.

Now associating each particle with the spin coordinate which can achieve the value either +1 or -1 and magnetic moment μ , a partition function can be written in the following manner. If an external magnetic field H is applied parallel to the c -axis of the crystal having the central atom in the A layer, then the partition function in the A layer is

$$Z_A = \sum_{\alpha_1=\pm 1} \sum_{\alpha_2=\pm 1} \dots \sum_{\alpha_8=\pm 1} \sum_{\alpha_9=\pm 1} \exp[(\mu \cdot H/kT) \alpha_1 + (\mu \cdot H_A/kT) \cdot (\alpha_1 + \alpha_2 + \dots + \alpha_8) + (\mu \cdot H_B/kT)(\alpha_9 + \alpha_{10} + \dots + \alpha_{16}) + (C/kT) \alpha_1 (\alpha_1 + \alpha_2 \dots + \alpha_8) - (C'/kT) \alpha_1 (\alpha_9 + \alpha_{10} + \dots + \alpha_{16})] \quad (8.1)$$

where H_A and H_B are effective magnetic field in layers A and B; C and C' are coupling constants between the spins in the same layer and in the different layer, respectively, and k is Boltzman constant. Let

$$\begin{aligned} \mu \cdot H/kT &= E, \quad \mu \cdot H_A/kT = E_A, \quad \mu \cdot H_B/kT = E_B, \\ C/kT &= J, \quad C'/kT = J'. \end{aligned} \quad (8.2)$$

Substituting the equation (8.2) into (8.1) and after a few operations, we obtain

$$\begin{aligned} Z_A &= \sum_{\alpha_1=\pm 1} \sum_{\alpha_2=\pm 1} \dots \sum_{\alpha_8=\pm 1} \sum_{\alpha_9=\pm 1} \sum_{\alpha_{10}=\pm 1} \dots \sum_{\alpha_{16}=\pm 1} \exp[E \alpha_1 + E_A (\alpha_1 + \dots + \alpha_8) + E_B (\alpha_9 + \dots + \alpha_{16}) + J \alpha_1 (\alpha_1 + \dots + \alpha_8) - J' \alpha_1 (\alpha_9 + \dots + \alpha_{16})] \\ &= e^E [2 \cosh(E_A + J)]^8 [2 \cosh(E_B - J')]^8 \\ &\quad + e^{-E} [2 \cosh(E_A - J)]^8 [2 \cosh(E_B + J')]^8 \\ &= Z_A^+ + Z_A^- \end{aligned} \quad (8.3)$$

where Z_A^+ and Z_A^- are relative probabilities for the spin $\alpha_1 = +1$ and $\alpha_1 = -1$.

For the equation with asterisk mark hereafter, a detailed derivation is given in the appendix section.

The average spin state of ϕ is then

$$\langle \phi \rangle_{av.} = \frac{Z_A^+ - Z_A^-}{Z_A}. \quad (8.4)^*$$

The partition function for one of the atoms, $j = 1, 2, \dots, 8$, in the layer A may be written as

$$Z_A = \prod_{j=1}^8 e^{E_{Aj} \phi_j}.$$

If the logarithm of the both sides is taken, it becomes

$$\ln Z_A = \sum_{j=1}^8 E_{Aj} \phi_j = 8 E_A \phi.$$

Therefore,

$$\langle \phi \rangle_{av.} = \frac{1}{8} \frac{\partial}{\partial E_A} \ln Z_A = \frac{1}{8 Z_A} \frac{\partial}{\partial E_A} Z_A \quad (8.5)$$

Substitution of equation (8.3) into (8.5) gives

$$\langle \phi \rangle_{av.} = \frac{1}{Z_A} [Z_A^+ \tanh(E_A + J) + Z_A^- \tanh(E_A - J)]. \quad (8.6)^*$$

The condition for $\langle \phi \rangle = \langle \phi_j \rangle$ can be derived then from the relation of equations (8.4) and (8.6) as follows

$$\frac{Z_A^+ - Z_A^-}{Z_A} = \frac{1}{Z_A} [Z_A^+ \tanh(E_A + J) + Z_A^- \tanh(E_A - J)]. \quad (8.7)$$

Substituting the values of Z_A^+ and Z_A^- into equation (8.7) and rearranging the terms, we obtain

$$\left[\frac{\cosh(E_A + J)}{\cosh(E_A - J)} \right]^7 \left[\frac{\cosh(E_b - J')}{\cosh(E_b + J')} \right]^8 = e^{2(E_A - E)}. \quad (8.8)^*$$

Similarly, we obtain for the central atom on the B lattice

$$\left[\frac{\cosh(E_b + J)}{\cosh(E_b - J)} \right]^7 \left[\frac{\cosh(E_a - J')}{\cosh(E_a + J')} \right]^8 = e^{2(E_b - E)}. \quad (8.9)$$

In the absence of an external field, i.e., $H = 0$, it is possible to obtain two solutions from the equations (8.8) and (8.9). Namely, $E_a = E_b = 0$ at any temperature and $E_a = -E_b$ below the Néel or Curie temperature. Since we are principally interested in the latter case, substituting the relation $E_a = -E_b$ into (8.8), we obtain

$$\left[\frac{\cosh(E_a + J)}{\cosh(E_a - J)} \right]^7 \left[\frac{\cosh(-E_a - J')}{\cosh(-E_a + J')} \right]^8 = e^{2E_a}. \quad (8.10)$$

A further manipulation reduces this equation to one of the most important equations,

$$7 \tanh J + 8 \tanh J' = 1. \quad (8.11)^*$$

To evaluate J and J' , we must have another equation which contains J and J' . To this end, refer to equation (8.1), and rewrite the partition function in the following way:

$$Z_A = \sum_{\sigma_a = \pm 1} \sum_{\sigma_b = \pm 1} (e^{E \sigma_a} + E_a \sigma_a + J \sigma_a \sigma_b) [2 \cosh(E_a + J \sigma_a)]^7 [2 \cosh(E_b - J' \sigma_b)]^8. \quad (8.12)^*$$

The relative probabilities Z_{A+-} when $\sigma_a = +1$, and $\sigma_b = -1$, Z_{A++} when $\sigma_a = +1$ and $\sigma_b = +1$, and Z_{A--} when $\sigma_a = -1$ and $\sigma_b = -1$ can be obtained from the equation (8.12) as shown below:

$$\begin{aligned} Z_{A+-} &= \langle P_{A+-} \rangle = e^{E - E_a - J} [2 \cosh(E_a + J)]^7 [2 \cosh(E_b - J')]^8, \\ Z_{A++} &= \langle P_{A++} \rangle = e^{E + E_a + J} [2 \cosh(E_a + J)]^7 [2 \cosh(E_b - J')]^8, \\ Z_{A--} &= \langle P_{A--} \rangle = e^{-E - E_a + J} [2 \cosh(E_a - J)]^7 [2 \cosh(E_b + J')]^8. \end{aligned} \quad (8.13)$$

The quasi-chemical relation in the same layer is then given

by

$$\frac{\langle P_{A+-} \rangle^2}{\langle P_{A++} \rangle \langle P_{A--} \rangle} = \frac{\langle P_{B+-} \rangle^2}{\langle P_{B++} \rangle \langle P_{B--} \rangle} = 4 e^{-4J}. \quad (8.14)^*$$

Again, from equation (8.1), we obtain

$$Z_A = \sum_{\sigma_a = \pm 1} \sum_{\sigma_b = \pm 1} e^{E_{\sigma_a} + E_{\sigma_b} - J' \sigma_a \sigma_b} [2 \cosh(E_a + J \sigma_a)]^7 [2 \cosh(E_b - J' \sigma_b)]^8 \quad (8.15)$$

As before the relative probabilities for various spin couplings between two layers are then

$$\begin{aligned} Z_{++} &= \langle Q_{++} \rangle = e^E + E_b - J' [2 \cosh(E_a + J)]^7 [2 \cosh(E_b - J')]^8, \\ Z_{+-} &= \langle Q_{+-} \rangle = e^E - E_b + J' [2 \cosh(E_a + J)]^7 [2 \cosh(E_b - J')]^8, \\ Z_{-+} &= \langle Q_{-+} \rangle = e^{-E} + E_b + J' [2 \cosh(E_a - J)]^7 [2 \cosh(E_b + J')]^8, \\ Z_{--} &= \langle Q_{--} \rangle = e^{-E} - E_b - J' [2 \cosh(E_a - J)]^7 [2 \cosh(E_b + J')]^8. \end{aligned} \quad (8.16)$$

From (8.16) the quasi-chemical relations between two layers are then given by the following equation,

$$\frac{\langle Q_{++} \rangle \langle Q_{--} \rangle}{\langle Q_{+-} \rangle \langle Q_{-+} \rangle} = e^{-4J}. \quad (8.17)$$

The following relations also exist between the layers.

$$2 P_{A++} + P_{A+-} = 8 N_{A+}, \quad 2 P_{A--} + P_{A-+} = 8 N_{A-}, \quad (8.18)$$

$$2 P_{B++} + P_{B+-} = 8 N_{B+}, \quad 2 P_{B--} + P_{B-+} = 8 N_{B-}, \quad (8.19)$$

$$Q_{++} + Q_{+-} = 8 N_{A+}, \quad Q_{--} + Q_{-+} = 8 N_{A-}, \quad (8.20)$$

$$Q_{++} + Q_{-+} = 8 N_{B+}, \quad Q_{--} + Q_{+-} = 8 N_{B-}, \quad (8.21)$$

$$N_{A+} + N_{A-} = N_A = N/2, \quad N_{B+} + N_{B-} = N_B = N/2. \quad (8.22)$$

where $N_{A\pm}$ and $N_{B\pm}$ are numbers of positive and negative sites in the layer A and B, respectively; N_A and N_B are numbers of sites in the A and B layers and N is a total number of sites.

Using the above relations, the configurational energy of the system W can be expressed in terms of five independent parameters as follows:

$$\begin{aligned} W(N_{A+}, N_{B+}, \langle P_{A+-} \rangle, \langle P_{B+-} \rangle, \langle Q_{+-} \rangle; H, T) \\ = -C(P_{A++} + P_{A--} - P_{A+-} - P_{B++} - P_{B--} + P_{B+-}) \\ + C'(Q_{++} - Q_{--} - Q_{+-} - Q_{-+}) \end{aligned}$$

$$\begin{aligned}
& - \mu_- H(N_{A+} + N_{B+} - N_{A-} - N_{B-}) \\
& = -4N(C-C') + 2C(P_{A+-} - P_{B+-}) \\
& \quad - 2C [2Q_{+-} - 8(N_{A+}N_{B+})] \\
& - \mu_- [2(N_{A+} + N_{B+}) - N].
\end{aligned} \tag{8.23}^*$$

The configurational free energy F can be evaluated by the following well known thermodynamic relation:

$$\begin{aligned}
& \langle W(N_{A+}, N_{B+}, \langle P_{A+-} \rangle, \langle P_{B+-} \rangle, \langle Q_{+-} \rangle; H, T) \rangle \\
& = \frac{\partial [F(N_{A+}, N_{B+}; H, T)/T]}{\partial (1/T)}
\end{aligned} \tag{8.24}^*$$

Integration of equation (8.24) renders, in turn, problems of evaluating the following two terms in equation (8.25).

$$\frac{F}{T} = \left(\frac{F}{T} \right)_{\infty} - \int \frac{W}{T^2} dT. \tag{8.25}$$

The first term on the right hand side of the equation is an integration constant and is evaluated by the following thermodynamic relation:

$$\begin{aligned}
\left(\frac{F}{T} \right)_{\infty} &= \left(\frac{\langle W \rangle}{T} \right)_{\infty} - (S)_{T=\infty} \\
&= -k \log \frac{N/2!}{N_{A+}! (N/2 - N_{A+})!} \cdot \frac{N/2!}{N_{B+}! (N/2 - N_{B+})!}
\end{aligned}$$

By Stirling's approximation, this can be rewritten as:

$$\begin{aligned}
\left(\frac{F}{T} \right)_{\infty} &= (Nk/4) [(1+s)\log(1+s) + (1-s)\log(1-s) \\
& \quad + (1+s)\log(1+s) + (1-s)\log(1-s) - 4 \log 2], \tag{8.26}^*
\end{aligned}$$

where s and s' are order parameters and will be introduced in the following equations:

$$N_{A+} = \frac{N(1+s)}{4}, \quad N_{B+} = \frac{N(1+s')}{4}, \tag{8.27}$$

where

$$0 \leq s \leq 1 \text{ and } -1 \leq s' \leq 1.$$

Using equations (8.14), (8.18), and (8.22), the following quantities can be expressed as:

$$\langle P_{A+-} \rangle = 2N \frac{[1 + (1 - s^2)(e^{4C/kT} - 1)]^{1/2} - 1}{e^{4C/kT} - 1}, \quad (8.28)^*$$

$$\langle P_{B+-} \rangle = 2N \frac{[1 + (1 - s'^2)(e^{4C/kT} - 1)]^{1/2} - 1}{e^{4C/kT} - 1}. \quad (8.29)^*$$

Similarly, from equations (8.10), (8.15), (8.16), and (8.20),

$$\begin{aligned} \langle Q_{+-} \rangle &= N[(2 + s - s') + 2/(e^{4C'/kT} - 1)] \\ &\quad - N[(2 + s - s') + \frac{2}{e^{4C'/kT} - 1}]^2 \\ &\quad - \frac{4e^{4C'/kT}}{e^{4C'/kT} - 1} (1 + s)(1 - s')]^{1/2}. \end{aligned} \quad (8.30)^*$$

Upon substitution of equations (8.27), (8.28), (8.29), and (8.30) into equation (8.23), it becomes:

$$\begin{aligned} &W(N_{A+}, N_{B+}, P_{A+-}, P_{B+-}, Q_{+-}, H, T) \\ &= 4N(C - C') + 2C(P_{A+-} + P_{B+-}) \\ &\quad - 2C'[2Q_{+-} - 8(N_{A+} - N_{B+})] \\ &\quad - \mu H[2(N_{A+} + N_{B+}) - N] \\ &= 4N(C - C') - 2C2N \left\{ \frac{[1 + (1 - s^2)(e^{4C/kT} - 1)]^{1/2} - 1}{e^{4C/kT} - 1} \right\} \\ &\quad + 2C2N \left\{ \frac{[1 + (1 - s'^2)(e^{4C/kT} - 1)]^{1/2} - 1}{e^{4C/kT} - 1} \right\} \\ &\quad - 4C' \left\{ N(2 + s - s' + \frac{2}{e^{4C'/kT} - 1}) - N \left[(2 + s - s' + \frac{2}{e^{4C'/kT} - 1})^2 \right. \right. \\ &\quad \left. \left. - \frac{4e^{4C'/kT}}{e^{4C'/kT} - 1} (1 + s)(1 - s') \right]^{1/2} \right\} + 16C' \left\{ \frac{N(1 + s)}{4} - \frac{N(1 + s')}{4} \right\} \\ &\quad - \mu H \left\{ 2 \frac{N(1 + s) + N(1 + s')}{4} - N \right\} \end{aligned}$$

$$\begin{aligned}
&= -4N(C - C') + 4CN \left\{ \frac{[1 + (1 - s^2)(e^{4C/kT} - 1)]^{\frac{1}{2}} - 1}{e^{4C/kT} - 1} \right\} \\
&\quad + 4CN \left\{ \frac{[1 + (1 - s'^2)(e^{4C/kT} - 1)]^{\frac{1}{2}} - 1}{e^{4C/kT} - 1} \right\} \\
&\quad - 4C'N \left\{ \left[(2 + s - s' - \frac{2}{e^{4C'/kT} - 1}) \right] \right. \\
&\quad \left. - \left[(2 + s - s' + \frac{2}{e^{4C'/kT} - 1})^2 - \frac{4e^{4C'/kT}}{e^{4C'/kT} - 1} (1 + s)(1 - s') \right]^{\frac{1}{2}} \right\} \\
&\quad + 4C'N(s - s') - \frac{N\mu_0 H}{2} (s + s'). \tag{8.31}
\end{aligned}$$

From equations (8.25) and (8.31), we obtain

$$\begin{aligned}
&= \int \frac{\langle W \rangle}{T^2} dT \\
&= 4N(C - C') \int \frac{dT}{T^2} - 4CN \left\{ \int \frac{[1 + (1 - s^2)(e^{4C/kT} - 1)]^{\frac{1}{2}} - 1}{(e^{4C/kT} - 1) T^2} dT \right. \\
&\quad + \int \frac{[1 + (1 - s'^2)(e^{4C/kT} - 1)]^{\frac{1}{2}} - 1}{(e^{4C/kT} - 1) T^2} dT + 4C'N \int [2 + s - s' \\
&\quad + \frac{2}{e^{4C'/kT} - 1}] \frac{dT}{T^2} - 4C'N \int \left[(2 + s - s' + \frac{2}{e^{4C'/kT} - 1})^2 \right. \\
&\quad \left. - \frac{4e^{4C'/kT}}{e^{4C'/kT} - 1} (1 + s)(1 - s') \right]^{\frac{1}{2}} \frac{dT}{T^2} - 4C'N (s - s') \int \frac{dT}{T^2} \\
&\quad \left. + \frac{N\mu_0 H}{2} (s + s') \int \frac{dT}{T^2} \right\} \tag{8.32}
\end{aligned}$$

Integrating equation (8.32) as shown in the Appendix, the following result is obtained:

$$\begin{aligned}
&= \int \frac{\langle W \rangle}{T^2} dT \\
&= -4N(C - C')/T + kN \left\{ -2 \log \frac{t+1}{2} + (1+s) \log \frac{t+s}{1+s} \right. \\
&\quad + (1-s) \log \frac{t-s}{1-s} - 2 \log \frac{t'+1}{2} + (1+s') \log \frac{t'+s'}{1+s'} \\
&\quad + (1-s') \log \frac{t'-s'}{1-s'} \left. \right\} + 2kN \left\{ -\frac{(s-s')}{2} \log \right. \\
&\quad \frac{\sqrt{M} + (s-s'/2)m - (1-ss')/(s-s')}{1/(s-s')} - \log \frac{\sqrt{M} - (1-ss'/2)m - 1}{1-m} \\
&\quad + (s+s')/2 \log \\
&\quad \frac{\sqrt{M} + [(s+s')/2 - (1-ss')/(s-s')]m + (1+ss')/(s+s')}{1/(s-s')(1-m)} \left. \right\}
\end{aligned}$$

$$- \frac{N \mu_0 H}{2T} (s + s'), \quad (8.33)^*$$

where

$$\begin{aligned} t^2 &= 1 + (1 - s^2)(e^{4C/kT} - 1), \\ t'^2 &= 1 + (1 - s'^2)(e^{4C'/kT} - 1), \\ M(m) &= \frac{(s - s')^2}{-4} m - (1 - ss')m + 1, \\ m &= 1 - e^{-4C'/kT}. \end{aligned} \quad (8.34)$$

Now combining equations (8.25), (8.26), and (8.33), the configurational free energy F can be expressed as follows:

$$\begin{aligned} F &= \frac{NkT}{4} \{ (1+s)\log(1+s) + (1-s)\log(1-s) + (1+s')\log(1+s') \\ &\quad + (1-s')\log(1-s') - 4 \log 2 \} \\ &\quad - 4N(C - C')/T - \frac{N \mu_0 H}{2T} (s + s') + kN \{ -2 \log \frac{t+1}{2} \\ &\quad + (1+s)\log \frac{t+s}{1+s} + (1-s)\log \frac{t-s}{1-s} - 2 \log \frac{t'+1}{2} \\ &\quad + (1+s')\log \frac{t'+s'}{1+s'} + (1-s')\log \frac{t'-s'}{1-s'} \} \\ &\quad + 2kN \{ - \frac{(s-s')}{2} \log \frac{\sqrt{M} - (s-s')m/2 - (1-ss')/(s-s')}{1/(s-s')} \\ &\quad - \log \frac{\sqrt{M} - (1-ss')m/2 + 1}{1-m} + \frac{s+s'}{2} \log \\ &\quad \frac{\sqrt{M} + [(s+s')/2 - (1+ss')/(s+s')]m + (1+ss')/(s+s')}{1/(s+s')(1-m)} \} \\ &= \frac{NkT}{4} \{ -16(C/kT - C'/kT) - 2 \mu_0 H(s+s')/kT + [(1+s)\log(1+s) \\ &\quad + (1-s)\log(1-s) + (1+s')\log(1+s') + (1-s')\log(1-s') \\ &\quad - 4 \log 2] + 4[(1+s)\log \frac{t+s}{1+s} + (1-s)\log \frac{t-s}{1-s} - 2 \log \frac{t+1}{2} \\ &\quad + (1+s')\log \frac{t'+s'}{1+s'} + (1-s')\log \frac{t'-s'}{1-s'} - 2 \log \frac{t'+1}{2}] \\ &\quad - 8 \{ \log \frac{\sqrt{M} - (1-ss')m/2 + 1}{1-m} + \frac{(s-s')}{2} \log \\ &\quad \frac{\sqrt{M} - (s-s')m/2 - \frac{1-ss'}{s-s'}}{1/(s-s')} - \frac{s-s'}{2} \log \\ &\quad \frac{\sqrt{M} + [(s-s')/2 - (1-ss')/(s-s')]m + (1+ss')/(s+s')}{(1/s-s')(1-m)} \} \} \end{aligned}$$

Expanding equation (8.35) in terms of m , taking up to m^2 terms, and rearranging, we obtain:

$$\begin{aligned}
 & F(s, s', H, T) \\
 = & -kN(C - C') - \frac{N}{2} \mu_0 H(s + s') \\
 & - \frac{3NkT}{4} \left\{ (1+s)\log(1+s) + (1-s)\log(1-s) + (1+s')\log(1+s') \right. \\
 & + (1-s')\log(1-s') - 4\log 2 \left. \right\} + NkT \left\{ (1+s)\log(t+s) \right. \\
 & + (1-s)\log(t-s) - 2\log(t+1) + (1+s')\log(t'+s') \\
 & + (1-s')\log(t'-s') - 2\log(t'+1) \left. \right\} + NkT \left\{ (1+ss')m \right. \\
 & + \frac{m^2}{8} [4(1+ss') - (1-s^2)(1-s'^2)] + \dots \left. \right\} + 2NkT \log(1-m), \quad (8.36)^*
 \end{aligned}$$

From minimization conditions, $\frac{\partial F}{\partial s} = \frac{\partial F}{\partial s'} = 0$, we obtain

$$\begin{aligned}
 -\frac{\mu_0 H}{kT} - \frac{3}{2} \log \frac{1+s}{1-s} + 2 \log \frac{t+s}{t-s} + \frac{1}{2} m^2 s + m(m+2)s' - \frac{1}{2} ss'm^2 &= 0, \\
 -\frac{\mu_0 H}{kT} - \frac{3}{2} \log \frac{1+s'}{1-s'} + 2 \log \frac{t'+s'}{t'-s'} + \frac{1}{2} m^2 s' + m(m+2)s &= 0, \\
 -\frac{1}{2} s^2 s' m^2 &= 0. \quad (8.37)^*
 \end{aligned}$$

Now applying the following Néel temperature conditions to the equation (3.27), we obtain

$$\left(\frac{\partial^2 F}{\partial s \partial s'} \right)^2 - \left(\frac{\partial^2 F}{\partial s^2} \right) \left(\frac{\partial^2 F}{\partial s'^2} \right) = 0,$$

$$\left(\frac{\partial^2 F}{\partial s^2} \right) > 0, \quad \frac{\partial F}{\partial s} = \frac{\partial F}{\partial s'} = 0,$$

$$s = s' = 0. \quad (8.38)$$

another important equation is obtained:

$$4e^{-2C/kT} - 2e^{-4C'/kT} - 5 = 0. \quad (8.39)^*$$

Now we are in a position to be able to evaluate the ferro- and antiferromagnetic coupling constants C and C' from equation (8.11) and (8.39), provided the Néel temperature T_N is known. It is customary to evaluate these constants semi-empirically as

done by Yomosa.²² It is, however, in the present calculation shown that these constants can be estimated without recourse to the experimental data by solving equations (8.11) and (8.39) graphically.

In order to facilitate the calculations, the equations (8.11) and (8.39) are transformed into the following forms:

$$J' = \arctan \frac{1}{8}(1 - 7 \tanh J), \quad (8.11)$$

$$J' = -0.578 \log(2.5 - 2e^{-2J}), \quad (8.39)$$

where

$$J = C/kT \text{ and } J' = C'/kT$$

Equations (8.11) and (8.39) are plotted as shown in Figure 2 according to the data tabulated in Table 1. From the graph J and J' values are found to be 0.025 and 0.122, respectively. Since we know the Néel temperature $T_N = 78^\circ \text{K}$ for FeF_2 from the heat capacity and magnetic susceptibility measurements,¹⁸ the ferromagnetic and antiferromagnetic coupling constants C and C' can be estimated from the relations $J = C/kT_N$ and $J' = C'/kT_N$. The calculation gives the value of 1.95 k for C and of 9.52 k for C' .

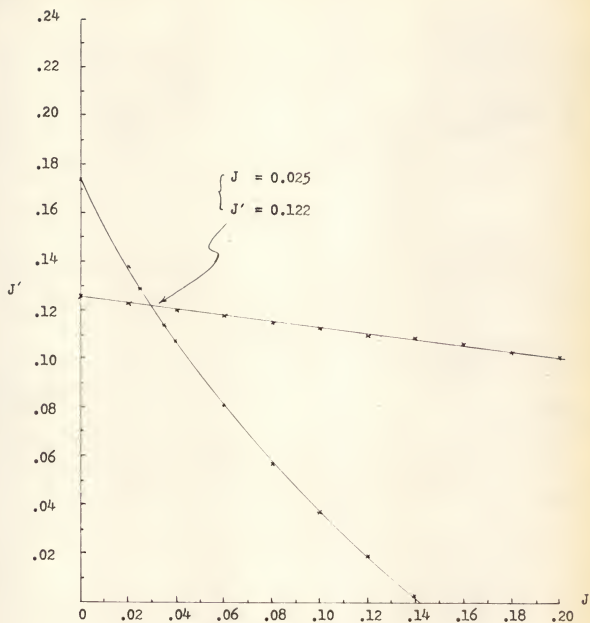
Exactly the same type of calculations were carried out for the isomorphic crystalline compounds MnF_2 and CoF_2 and their respective coupling constants are tabulated in Table 2. The relations between the magnitude of the coupling constants and the Néel temperature are shown in the Figure 3.

FeCl_2

In his theoretical paper on FeCl_2 , Yomosa²² evaluated semi-empirically the coupling constants to be 4.30 k for C and 0.43 k

Table 2
Data for the Graphical Solution

$J' = \text{arc tanh } \frac{1}{8}(1 - 7 \tanh J)$		$J' = -0.578 \log(2.5 - 2e^{-2J})$	
J	J'	J	J'
0.000	0.126	0.000	0.174
0.020	0.123	0.020	0.138
0.040	0.120	0.025	0.129
0.060	0.118	0.030	0.123
0.080	0.115	0.035	0.114
0.100	0.113	0.040	0.107
0.120	0.110	0.060	0.081
0.140	0.109	0.080	0.057
0.160	0.106	0.100	0.037
0.180	0.103	0.120	0.019
0.200	0.101	0.140	0.003

Figure 2. FeF_2 .

for C' which correspond to the Néel temperature $T_N = 24^\circ\text{K}$.

The magnetic entropy at this transition temperature, however, does not account all the spin multiplicity ($2S + 1$), i.e., it amounts to only $R \ln 2$. This fact clearly indicates a possible presence of the second transition temperature. In an effort to find such a second transition point it was decided to repeat the calculations for the FeCl_2 . Two equations obtained by Yomosa²² were solved graphically as shown in Figure 4 and two sets of roots were found, one of which corresponds to $T_N = 24^\circ\text{K}$. Assuming the coupling constants $C = 4.30 \text{ k}$ and $C' = 0.432 \text{ k}$ obtained at $T_N = 24^\circ\text{K}$ remain unchanged over the temperature range, the second transition temperature was calculated from the relation $J = C/kT_N$ and T_{N2} was obtained to be 27°K .

Whether the second transition temperature we found has a real significance or not will be discussed in detail in the following chapter.

As in the previous cases, for the isomorphic crystalline substance NiCl_2 , and CoCl_2 with FeCl_2 , the coupling constants C and C' are evaluated and tabulated in the Table 3 and the relation between the Néel temperature, T_N , and the coupling constants, C and C' , are illustrated in the Figure 3.

Table 3

Ferro and Antiferromagnetic Coupling Constants
and Their Respective Neel Temperature

Compound	Crystal Structure	$T_N(^{\circ}\text{K})$	C	C'
FeF_2	Rutile	78.4	1.95 k	9.52 k
MnF_2	"	66.5	1.66 k	8.11 k
CoF_2	"	37.7	.943 k	4.60 k
FeCl_2	Hexagonal close- packed	24.0	4.30 k	.432 k
CoCl_2	"	25.0	4.48 k	.450 k
NiCl_2	"	52.0	9.31 k	.936 k

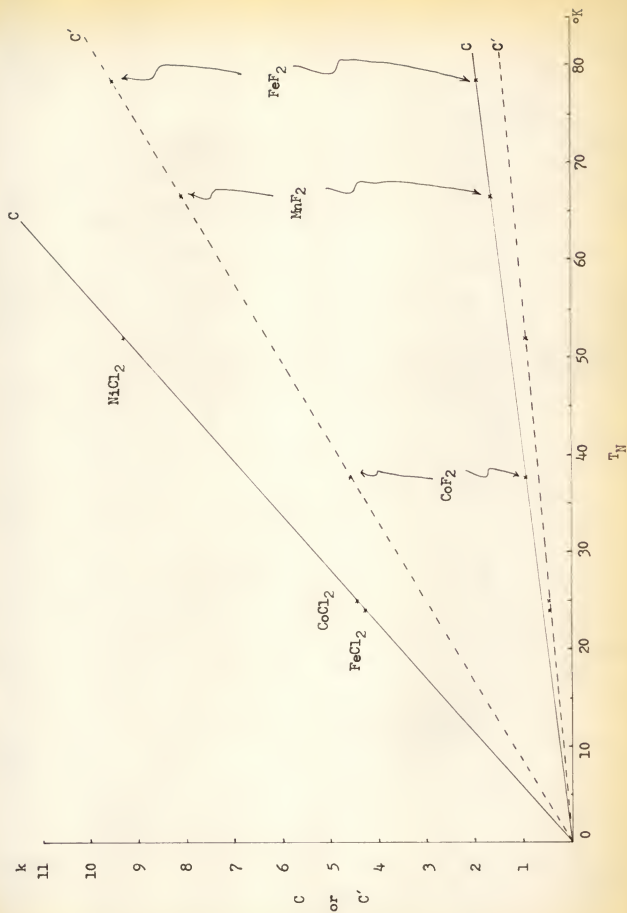


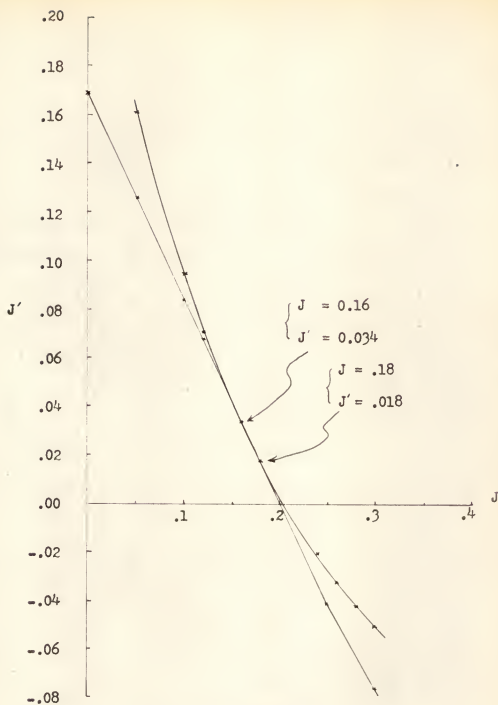
Figure 3.

Table 4

Data for the Graphical Solution

$$J' = \text{arc tanh } \frac{1}{6}(1 - 5 \tanh J) \quad J' = 0.58[(0.18 - \log(3.5 - 3e^{-2J}))]$$

J	J'	J	J'
0.000	0.169	0.000	0.285
0.050	0.126	0.050	0.161
0.100	0.084	0.100	0.095
0.120	0.068	0.120	0.071
0.140	0.051	0.149	0.052
0.160	0.034	0.160	0.034
0.180	0.018	0.180	0.018
0.200	0.002	0.200	0.004
0.250	-0.041	0.220	-0.009
0.300	-0.076	0.240	-0.020
		0.260	-0.032
		0.280	-0.042

Figure 4. FeCl_2 .

CHAPTER IX

RESULTS AND DISCUSSION

Frequent references will be made to Table 3 and Figure 3 in the following discussions. The first thing to be noticed in Figure 3 is that the transition temperature T_N rises as the magnitudes of the coupling constants increase and for the isomorphic crystalline compounds the plots of C versus T_N or of C' versus T_N form straight lines. These lines also converge to zero at 0°K, confirming Van Vleck's theory on antiferromagnetism. A second point to be considered is the fact that in the FeF_2 series C' 's have larger values than C indicating antiferromagnetic couplings were much greater than ferromagnetic couplings, while in FeCl_2 series the order is reversed, i.e., C 's have much greater values than the antiferromagnetic coupling constants, C' . This reversed situation in the two different crystalline structures is reflected as higher transition temperatures for the FeF_2 series and lower transition temperatures for the FeCl_2 series.

Therefore, it can be concluded that the MnF_2 series have strong antiferromagnetic coupling between the spins and the FeCl_2 series have, on the other hand, strong ferromagnetic spin couplings. These agree very well with our expectations.

As to the existence of the second transition temperature, some experimental evidence can be cited which provides a strong support

for this. According to Stout, et al.,¹⁸ the magnetic entropy observed for FeCl_2 at first transition temperature, $T_N = 24^\circ\text{K}$, does not account the expected value of $R \ln(2S + 1) = R \ln 5$ but only $R \ln 2$. R. B. Murray,³⁰ on the other hand, observed two transitions temperatures $T_{N1} = 1.81^\circ\text{K}$ and $T_{N2} = 1.96^\circ\text{K}$ for MnCl_2 and was able to account for the magnetic entropy $R \ln 6$ by summing up the values at these two transition points. The next question to be asked is then why the second transition temperature has not been found for FeCl_2 in spite of the fact that the first transition occurs at 24°K and the predicted second transition appears at 27°K which is much higher than those temperatures observed for MnCl_2 case.

A partial answer to this may be found, without too elaborate treatment, if we consider how the magnetic entropy contribution is separated from the lattice entropy contribution. For MnF_2 , FeF_2 , and CoF_2 , for example, Stout used diamagnetic as well as isomorphous crystalline substance ZnF_2 in the evaluation of magnetic entropy. Worded differently, the magnetic entropy is the difference of total entropy of each MnF_2 , FeF_2 , and CoF_2 minus that of ZnF_2 which has only lattice contribution to the entropy, for it has a closed 3d-shell or a $3d^{10}$ configuration. Although it appears to be a simple matter to separate and identify the two different contributions to the entropy, such identification is greatly hampered by the fact that the lattice contribution is considerably large even at low temperatures, so that the magnetic contribution is quite often obscured by the lattice contribution.

The following example, however, will show the correctness and validity of the second transition phenomenon. For instance, in MnCl_2 which is isomorphic with FeCl_2 in crystalline structure, the ferromagnetic coupling constant C is estimated to be 0.326 k at first transition temperature $T_{N1} = 1.81$ °K. Now assuming the ferromagnetic coupling constant C does not change over not too wide temperature range, the second transition temperature T_{N2} is evaluated to be 2.03 °K. This is an excellent agreement with experimentally observed second transition temperature $T_{N2} = 1.96$ °K.

Stout¹⁸ also predicted in his paper the possibility of isolating the remaining magnetic entropy for FeCl_2 over a temperature range higher than $T_{N1} = 24$ °K. All this evidence suggests that at the second transition temperature $T_{N2} = 27$ °K the remaining magnetic entropy contribution would appear. To verify this, further refined experimental results must be obtained. The difficulty with measurements on FeCl_2 is due to the much larger contributions of lattice entropy at the expected transition temperature. This difficulty does not exist for MnCl_2 where the transition temperatures are very low.

CHAPTER X

SUMMARY

A statistical mechanical method based on the "Ising model" was applied to two crystalline structures including close-packed hexagonal substances such as FeCl_2 , MnCl_2 , NiCl_2 , and rutile structural substances such as FeF_2 , MnF_2 , and CoF_2 , etc.

The most significant result of this investigation was the theoretical prediction of the second Néel transition temperature.

As expected, it was found that the ferromagnetic couplings were much stronger than the antiferromagnetic for the series of compounds FeCl_2 , CoCl_2 , and NiCl_2 . In the same series the transition temperature rises as the magnitude of the antiferromagnetic coupling constants increases. On the other hand, in the series MnF_2 , FeF_2 , and CoF_2 , the antiferromagnetic couplings were much larger than ferromagnetic. This has the effect of elevating the transition temperatures much more than for the corresponding compounds in the close-packed hexagonal crystals. The transition temperature rises as the magnitude of the antiferromagnetic coupling constants increases, as in the previous case.

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APPENDIX

$$Z_A = \sum_{q_1=1} \sum_{q_2=1} \dots \sum_{q_{n-1}=1} \sum_{q_n=1} e^{E_A} (q_1 + \dots + q_n) + E_b (q_1 + \dots + q_n) + J q_1 (q_2 + \dots + q_n) - J' q_1' (q_2 + \dots + q_n) \quad (8.3)^*$$

$$\begin{aligned} &= \sum_{q_1=1} e^{E_A} \prod_{j=1}^n \left[\sum_{q_j=1} e^{(E_a + J)} \cdot \prod_{j=1}^n (E_b - J' q_j') q_j \right] \\ &= e^E \prod_{j=1}^n \left[e^{(E_a + J)} + e^{-(E_a + J)} \right] \cdot \prod_{j=1}^n \left[e^{(E_b - J')} + e^{-(E_b - J')} \right] \\ &\quad + e^{-E} \prod_{j=1}^n \left[e^{(E_a - J)} + e^{-(E_a - J)} \right] \cdot \prod_{j=1}^n \left[e^{(E_b + J)} + e^{-(E_b + J)} \right] \\ &= e^E [2 \cosh(E_a + J)]^n [2 \cosh(E_b - J')]^n + e^{-E} [2 \cosh(E_a - J)]^n [2 \cosh(E_b + J')]^n \\ &= Z_A^+ + Z_A^- \quad (8.3)^* \end{aligned}$$

$$(8.4)^*$$

From equation (8.3)*

$$\begin{aligned} \ln Z_A &= q_1 E + \ln \{ [2 \cosh(E_a + J)]^n [2 \cosh(E_b - J')]^n + [2 \cosh(E_a - J)]^n [2 \cosh(E_b + J')]^n \} \\ q_1 E &= \ln Z_A - \ln \{ [2 \cosh(E_a + J)]^n [2 \cosh(E_b - J')]^n + [2 \cosh(E_a - J)]^n [2 \cosh(E_b + J')]^n \} \\ \langle q_1 \rangle_{av.} &= \frac{\partial}{\partial E} \ln \frac{Z_A}{[2 \cosh(E_a + J)]^n [2 \cosh(E_b - J')]^n + [2 \cosh(E_a - J)]^n [2 \cosh(E_b + J')]^n} \end{aligned}$$

Let $X = [2 \cosh(E_a + J)]^n [2 \cosh(E_b - J')]^n + [2 \cosh(E_a - J)]^n [2 \cosh(E_b + J')]^n$ then,

$$\begin{aligned} \langle q_1 \rangle_{av.} &= \frac{\partial}{\partial E} \ln \frac{Z_A}{X} \frac{\partial X}{\partial E} \left\{ \frac{Z_A}{X} \right\} \\ &= \frac{X}{Z_A} \frac{\partial X}{\partial E} \frac{Z_A}{X} - \frac{Z_A}{X} \frac{\partial X}{\partial E} \frac{Z_A}{X} \end{aligned}$$

$$\begin{aligned}
&= \frac{X}{Z_A} \frac{X}{X^2} \frac{e^{E_a}}{X} = \frac{e^{E_a}}{Z_A} \\
&= \frac{e^{Z_A}}{Z_A} = \frac{(Z_A^+ + Z_A^-)}{Z_A} \\
&= \frac{Z_A^+ - Z_A^-}{Z_A}
\end{aligned}$$

(8.4)*

(8.6)*

Starting from equation (8.5)

$$\begin{aligned}
\langle \varphi \rangle_{av.} &= \frac{1}{8Z_A} \frac{\partial}{\partial E_a} \left\{ e^E [2\cosh(E_a + J)]^8 [2\cosh(E_b - J')]^8 + e^{-E} [2\cosh(E_a - J)]^8 [2\cosh(E_b + J')]^8 \right\} \\
&= \frac{1}{8Z_A} \left\{ 8e^E [2\cosh(E_a + J)]^7 [2\cosh(E_b - J')]^8 [2\sinh(E_a + J)] \right. \\
&\quad \left. + 8e^{-E} [2\cosh(E_a - J)]^7 [2\cosh(E_b + J')]^8 [2\sinh(E_a - J)] \right\} \\
&= \frac{1}{Z_A} \left\{ e^E [2\cosh(E_a + J)]^8 [2\cosh(E_b - J')]^8 \left[\frac{\sinh(E_a + J)}{\cosh(E_a + J)} \right] \right. \\
&\quad \left. + e^{-E} [2\cosh(E_a - J)]^8 [2\cosh(E_b + J')]^8 \left[\frac{\sinh(E_a - J)}{\cosh(E_a - J)} \right] \right\} \\
&= \frac{1}{Z_A} [Z_A^+ \tanh(E_a + J) + Z_A^- \tanh(E_a - J)]
\end{aligned}$$

(8.6)*

(8.8)*

Substituting the values of Z_A^+ and Z_A^- into the equation (8.7), we obtain

$$\begin{aligned}
&e^E [2\cosh(E_a + J)]^8 [2\cosh(E_b - J')]^8 - e^{-E} [2\cosh(E_a - J)]^8 [2\cosh(E_b + J')]^8 \\
&= e^E [2\cosh(E_a + J)]^7 [2\cosh(E_b - J')]^8 [2\sinh(E_a + J)]
\end{aligned}$$

$$+ e^E [2 \cosh(E_a - J)]^7 [2 \cosh(E_b + J')]^8 [2 \sinh(E_a - J)]$$

Rearranging the terms,

$$\begin{aligned} & e^E [2 \cosh(E_a + J)]^7 [2 \cosh(E_b - J')]^8 [\cosh(E + J) - \sinh(E_a + J)] \\ &= e^E [2 \cosh(E_a - J)]^7 [2 \cosh(E_b + J')]^8 [\cosh(E_a - J) + \sinh(E_a - J)] \end{aligned}$$

This can be written as:

$$\begin{aligned} & \left[\frac{\cosh(E_a + J)}{\cosh(E_a - J)} \right]^7 \left[\frac{\cosh(E_b - J)}{\cosh(E_b + J)} \right]^8 = \frac{e^E [\cosh(E_a - J) + \sinh(E_a - J)]}{e^E [\cosh(E_a + J) - \sinh(E_a + J)]} \\ &= \frac{e^E e^{(E_a - J)}}{e^E e^{-(E_a + J)}} = e^{2(E_a - E)} \end{aligned} \quad (8.8)^*$$

(8.11)*

Substituting $E_a = E_b$, and $E = 0$ into (8.8), we obtain

$$\left[\frac{\cosh(E_a + J)}{\cosh(E_a - J)} \right]^7 \left[\frac{\cosh(E_a - J')}{\cosh(E_a + J')} \right]^8 = e^{2E_a}$$

Taking logarithm of both sides,

$$7 \ln \left[\frac{\cosh(E_a + J)}{\cosh(E_a - J)} \right] + 8 \ln \left[\frac{\cosh(E_a + J')}{\cosh(E_a - J')} \right] = 2 E_a.$$

Since $\log x = 2 \left[\frac{x-1}{x+1} + \frac{1}{3} \left(\frac{x-1}{x+1} \right)^3 + \frac{1}{5} \left(\frac{x-1}{x+1} \right)^5 + \dots \right]$, for $x > 0$, expanding the first term of the left hand side,

$$7 \ln \left[\frac{\cosh(E_a + J)}{\cosh(E_a - J)} \right]$$

(8.8)*

$$\begin{aligned}
&= 14 \left\{ \frac{\cosh(E_a + J) - 1}{\cosh(E_a - J)} + \frac{1}{3} \left\{ \frac{\cosh(E_a + J) - 1}{\cosh(E_a + J)} + \frac{\cosh(E_a - J) + 1}{\cosh(E_a - J)} \right\} + \dots \right\} \\
&= 14 \left\{ \frac{\cosh(E_a + J) - \cosh(E_a - J)}{\cosh(E_a - J)} - \frac{\cosh(E_a - J)}{\cosh(E_a + J) + \cosh(E_a - J)} \right. \\
&\quad \left. + \frac{1}{3} \left[\frac{\cosh(E_a + J) - \cosh(E_a - J)}{\cosh(E_a + J) + \cosh(E_a - J)} \right]^3 + \dots \right\} \\
&= 14 \left\{ \frac{\cosh E_a \cosh J + \sinh E_a \sinh J - \cosh E_a \cosh J + \sinh E_a \sinh J}{\cosh E_a \cosh J + \sinh E_a \sinh J + \cosh E_a \cosh J - \sinh E_a \sinh J} \right. \\
&\quad \left. + \frac{1}{3} \left[\frac{2 \sinh E_a \sinh J}{2 \cosh E_a \cosh J} \right]^3 + \dots \right\} \\
&= 14 \left\{ \frac{\sinh E_a \sinh J + 1}{\cosh E_a \cosh J} \left(\frac{\sinh E_a \sinh J}{\cosh E_a \cosh J} \right)^3 + \dots \right\} \\
&= 14 \tanh J \left[\tanh E_a + \frac{1}{3} (\tanh E_a)^3 (\tanh J)^2 + \dots \right]
\end{aligned}$$

Now expanding the $\tanh E_a$ terms inside the bracket,

$$\begin{aligned}
&7 \ln \left\{ \frac{\cosh(E_a + J)}{\cosh(E_a - J)} \right\} \\
&= 14 \tanh J \left\{ E_a - \frac{E_a}{3} + \dots + \frac{1}{3} \left(E_a - \frac{E_a}{3} + \dots \right)^3 (\tanh J)^2 + \dots \right\} \\
&= 14 \tanh J \left\{ E_a - \frac{1}{3} E_a^3 (1 - \tanh^2 J) + \dots \right\} \\
&= 14 \tanh J \left\{ E_a - \frac{1}{3} E_a^3 \cosh^{-2} J + \dots \right\}
\end{aligned}$$

Similarly, the second term can be expanded as

$$8 \ln \left\{ \frac{\cosh(E_a + J')}{\cosh(E_a - J')} \right\} = 16 \tanh J' \left\{ E_a - \frac{1}{3} E_a^3 \cosh^{-2} J' + \dots \right\}$$

Substituting these two expansions into the original equations, we obtain

$$2 E_a = 14 \tanh J \left(E_a - \frac{E_a^2}{3} \cosh^{-2} J + \dots \right) + 16 \tanh J' \left[E_a - \frac{E_a^2}{3} \cosh^{-2} J + \dots \right]$$

Dividing through both sides by $2 E_a$,

$$1 = 7 \tanh J \left[1 - \frac{E_a^2}{3} \cosh^{-2} J + \dots \right] + 8 \tanh J' \left[1 - \frac{E_a^2}{3} \cosh^{-2} J + \dots \right]$$

Rearranging the terms,

$$E_a^2 \left(\frac{7 \tanh J}{3 \cosh^2 J} + \frac{8 \tanh J'}{3 \cosh^2 J'} + \dots \right) = 7 \tanh J + 8 \tanh J' - 1$$

$$E_a^2 = E_b^2 = \frac{3 \cosh J \cosh J'}{7 \cosh^3 J' \sinh J + 8 \cosh^3 J \sinh J'} (7 \tanh J + 8 \tanh J' - 1)$$

The Néel temperature, T_N , is then found from the relation,

$$7 \tanh J + 8 \tanh J' = 1$$

(8.12)*

(8.11)*

$$\begin{aligned} Z_A &= \sum_{\sigma_z=1} \dots \sum_{\sigma_z=1} \dots \sum_{\sigma_z=1} [E \sigma_z + E_a (\sigma_z + \dots + \sigma_z) + E_b (\sigma_z + \dots + \sigma_z)] \\ &\quad + J \sigma_z (\sigma_z + \dots + \sigma_z) - J' \sigma'_z (\sigma'_z + \dots + \sigma'_z)] \\ &= \sum_{\sigma_z=1} \sum_{\sigma'_z=1} E \sigma_z + E_a \sigma_z + J \sigma_z \sigma'_z \prod_{j=2}^N \left[\sum_{\sigma_z=1} e^{(E_a + J \sigma_z) \sigma_z} \right] \cdot \prod_{j=1}^N \left[\sum_{\sigma'_z=1} e^{(E_b - J' \sigma'_z) \sigma'_z} \right] \\ &= \sum_{\sigma_z=1} \sum_{\sigma'_z=1} [E \sigma_z + E_a \sigma_z + J \sigma_z \sigma'_z \prod_{j=2}^N \{ e^{(E_a + J \sigma_z)} + e^{-(E_a + J \sigma_z)} \} \cdot \prod_{j=1}^N \{ e^{(E_b - J' \sigma'_z)} + e^{-(E_b - J' \sigma'_z)} \}] \\ &= \sum_{\sigma_z=1} \sum_{\sigma'_z=1} [E \sigma_z + E_a \sigma_z + J \sigma_z \sigma'_z \{ 2 \cosh(E_a + J \sigma_z) \}^7 \{ 2 \cosh(E_b - J' \sigma'_z) \}^8] \end{aligned}$$

(8.12)*

(8.14)*

Including symmetry factor,

$$\begin{aligned}
\frac{\langle P_{A++} \rangle^2}{\langle P_{A++} \rangle \langle P_{A--} \rangle} &= 4 \frac{e^{2E} - 2E_a - 2J[2\cosh(E_a + J)]^{14} [2\cosh(E_b - J)]^{16}}{e^E + E_a + J - E - E_a + J[2\cosh(E_a + J)]^7 [2\cosh(E_b - J)]^8 [2\cosh(E_b + J')]^8} \\
&= 4e^{2E} - 2E_a - 4J \frac{[2\cosh(E_a + J)]^7 [2\cosh(E_b - J')]^8}{[2\cosh(E_a - J)]^7 [2\cosh(E_b + J')]^8} \\
&= 4e^{2E} - 2E_a - 4J \circ 2(E_a - E) \\
&= 4e^{4J} \\
&= \frac{\langle P_{B++} \rangle^2}{\langle P_{B++} \rangle \langle P_{B--} \rangle}
\end{aligned}$$

(8.14)*

(8.17)*

Using the relations of (8.16)

$$\begin{aligned}
\frac{\langle Q_{++} \rangle \langle Q_{--} \rangle}{\langle Q_{+-} \rangle \langle Q_{-+} \rangle} &= \frac{e^E + E_b - J' - E - E_b - J[2\cosh(E_a + J)]^7 [2\cosh(E_b - J')]^8 [2\cosh(E_a - J)]^7 [2\cosh(E_b + J')]^8}{e^E - E_b + J' - E + E_b + J[2\cosh(E_a + J)]^7 [2\cosh(E_b - J)]^8 [2\cosh(E_a - J)]^7 [2\cosh(E_b + J')]^8} \\
&= e^{4J'}
\end{aligned}$$

(8.17)*

(8.23)*

Using the relations (8.18), (8.19), and (8.22), each term of the equation (8.23) can be expressed in terms of independent variables, i.e.,

$$-C(P_{A++} + P_{A--} - P_{A+-} + P_{B++} + P_{B--} - P_{B+-})$$

$$\begin{aligned}
&= -C \{ (P_{A++} + P_{A+-} + P_{A-+} + P_{A--}) - 2 P_{A++} + (P_{B++} + P_{B+-} + P_{B-+} + P_{B--}) - 2 P_{B++} \} \\
&= -C \{ 4(N_{A+} + N_{A-}) + 4(N_{B+} + N_{B-}) - 2(P_{A++} + P_{B++}) \} \\
&= -4CN + 2C(P_{A++} + P_{B++})
\end{aligned}$$

Similarly, the second term can be expressed in terms of independent variables using the relations (8.20), (8.21), and (8.22),

$$\begin{aligned}
&C'(Q_{++} + Q_{--} - Q_{+-} - Q_{-+}) \\
&= C' \{ (Q_{++} + Q_{+-}) + (Q_{--} + Q_{-+}) - 2(Q_{+-} + Q_{-+}) \} \\
&= C' \{ 8(N_{A+} + N_{A-}) - 2(Q_{+-} + Q_{-+}) \} \\
&= C' \{ 4N - 2Q_{+-} - 2[8N_{B+} - Q_{++}] \} \\
&= C' \{ 4N - 2Q_{+-} - 2[8N_{B+} + Q_{+-} - 8N_{A+}] \} \\
&= C' \{ 4N - 4Q_{+-} - 2[8N_{B+} - 8N_{A+}] \}
\end{aligned}$$

Finally, the last term also can be written as follows, using the equation (8.22),

$$\begin{aligned}
&- \mu_0 H(N_{A+} + N_{B+} - N_{A-} - N_{B-}) \\
&= - \mu_0 H \{ (N_{A+} + N_{A-}) - 2N_{A-} + (N_{B+} + N_{B-}) - 2N_{B-} \} \\
&= - \mu_0 H \{ N - 2(N_{A-} + N_{B-}) \} \\
&= - \mu_0 H \{ N - 2[N_{A-} - N_{A+} + N_{B-} - N_{B+}] \} \\
&= - \mu_0 H \{ N - 2N + 2[N_{A+} + N_{B+}] \} \\
&= - \mu_0 H \{ 2[N_{A+} + N_{B+}] - N \}
\end{aligned}$$

Therefore,

$$W(N_{A+}, N_{B+}, P_{A++}, P_{B++}, Q_{+-}, H, T)$$

$$\begin{aligned}
&= -4CN + 2C(P_{A+} + P_{B+}) \\
&+ C' \{ 4N - 4Q_{A+} - 2[8N_{B+} - 8N_{A+}] \} \\
&- \mu_c H[2(N_{A+} + N_{B+}) - N] \\
&= -4N(C - C') + 2C(P_{A+} + P_{B+}) \\
&- 2C' \{ 2Q_{A+} - 8(N_{A+} - N_{B+}) \} \\
&- \mu_c H \{ 2(N_{A+} + N_{B+}) - N \}
\end{aligned}$$

(8.23)*

(8.26)*

$$\begin{aligned}
(F/T)_{\infty} &= -k \log \frac{N/2!}{N_{A+}!(N/2 - N_{A+})!} \frac{N/2!}{N_{B+}!(N/2 - N_{B+})!} \\
&= -k \{ \log(N/2!) - \log(N_{A+}!) - \log(N/2 - N_{A+})! + \log(N/2!) \} \\
&\quad - \log(N_{B+}!) - \log(N/2 - N_{B+})! \} \\
&= -k \left\{ \frac{N}{2} \log \frac{N}{2} - \frac{N}{2} - N_{A+} \log N_{A+} + N_{A+} - \left(\frac{N}{2} - N_{A+} \right) \log \left(\frac{N}{2} - N_{A+} \right) \right. \\
&\quad \left. + \left(\frac{N}{2} - N_{A+} \right) + \frac{N}{2} \log \frac{N}{2} - N_{B+} \log N_{B+} + N_{B+} - \left(\frac{N}{2} - N_{B+} \right) \log \left(\frac{N}{2} - N_{B+} \right) \right. \\
&\quad \left. + \left(\frac{N}{2} - N_{B+} \right) \right\} \\
&= -k \left\{ N \log \frac{N}{2} - N - \frac{N(1+s)}{4} \log \frac{N(1+s)}{4} + \frac{N(1+s)}{4} - \left[\frac{N}{2} - \frac{N(1+s)}{4} \right] \log \left[\frac{N}{2} - \frac{N(1+s)}{4} \right] \right. \\
&\quad \left. + \frac{N}{2} - \frac{N(1+s)}{4} - \frac{N(1+s')}{4} \log \frac{N(1+s')}{4} + \frac{N(1+s')}{4} - \left[\frac{N}{2} - \frac{N(1+s')}{4} \right] \right\} \\
&\quad \log \left\{ \frac{N}{2} - \frac{N(1+s')}{4} \right\}
\end{aligned}$$

$$\begin{aligned}
& -\frac{N(1+s')}{4} \log(1+s') - \frac{N(1-s')}{4} \log(1-s') \} \\
& = -k \left\{ N \log \frac{4}{2} - \frac{N(1+s)}{4} \log(1+s) - \frac{N(1-s)}{4} \log(1-s) \right. \\
& \quad \left. - \frac{N(1+s')}{4} \log(1+s') - \frac{N(1-s')}{4} \log(1-s') \right\} \\
& = \frac{Nk}{4} \{ (1+s) \log(1+s) + (1-s) \log(1-s) + (1+s') \log(1+s') \\
& \quad + (1-s') \log(1-s') - 4 \log 2 \}
\end{aligned}
\tag{8.26}^*$$

From equations (8.18) and (8.22),

$$\begin{aligned}
\frac{\langle P_{A+-} \rangle^2}{\langle P_{A++} \rangle \langle P_{A--} \rangle} &= \frac{\langle P_{A+-} \rangle^2}{\langle 4N_{A+} - 2P_{A+-} \rangle \langle 4N_{A-} - 2P_{A+-} \rangle} \\
&= \frac{\langle P_{A+-} \rangle^2}{\langle 16N_{A+}N_{A-} - 2P_{A+-}N_{A-} - 2P_{A+-}N_{A+} + P_{A+-}^2 \rangle} \\
&= \frac{\langle P_{A+-} \rangle^2}{16(N_{A+}N_{A-}) - 2P_{A+-}(N_{A+} + N_{A-}) + P_{A+-}^2}
\end{aligned}$$

Now using equation (8.14),

$$\langle P_{A+-} \rangle^2 = 4e^{-4J} [16(N_{A+}N_{A-}) - 2\langle P_{A+-} \rangle (N_{A+} + N_{A-}) + \frac{1}{4} \langle P_{A+-} \rangle^2]$$

Rearranging the terms,

$$(1 - e^{-4J}) \langle P_{A+-} \rangle^2 + 8(N_{A+} + N_{A-}) e^{-4J} \langle P_{A+-} \rangle - 64 e^{-4J} (N_{A+}N_{A-}) = 0$$

$$\begin{aligned}
& (s-l) \operatorname{sol} \frac{4}{(s-l)N} - (s+l) \operatorname{sol} \frac{4}{(s+l)N} - 4 \operatorname{sol} N - 4 \operatorname{sol} N + 2 \operatorname{sol} N - N \operatorname{sol} N \} x = \\
& \quad \{ (s-l) \operatorname{sol} \frac{4}{(s-l)N} - (s+l) \operatorname{sol} \frac{4}{(s+l)N} - N \operatorname{sol} \frac{2}{N} - 4 \operatorname{sol} N + \frac{2}{N} \operatorname{sol} N \} x = \\
& (s-l) \operatorname{sol} \frac{4}{(s-l)N} - (s+l) \operatorname{sol} \frac{4}{(s+l)N} - N \operatorname{sol} \frac{2}{N} + (s-l) \operatorname{sol} \frac{4}{(s-l)N} - \\
& \quad \{ (s-l) \operatorname{sol} \frac{4}{(s-l)N} - (s+l) \operatorname{sol} \frac{4}{(s+l)N} - (s+l) \operatorname{sol} \frac{4}{(s+l)N} + \frac{2}{N} \operatorname{sol} N \} x = \\
& (s+l) \operatorname{sol} \frac{4}{(s+l)N} - N \operatorname{sol} \frac{4}{(s-l)N} + (s+l)N - 4 \operatorname{sol} \frac{2}{N} + \frac{2}{N} \operatorname{sol} N \} x = \\
& \{ [(s-l)N] \operatorname{sol} \frac{4}{(s-l)N} - [(s+l)N] \operatorname{sol} \frac{4}{(s+l)N} - 4 \operatorname{sol} \frac{4}{(s-l)N} + 4 \operatorname{sol} \frac{4}{(s+l)N} + \\
& \quad \left[\frac{4}{(s-l)N} \right] \operatorname{sol} \frac{4}{(s-l)N} - \frac{4}{SN-N+SN+N} + \frac{4}{(s+l)N} \operatorname{sol} \frac{4}{(s+l)N} - N - \frac{2}{N} \operatorname{sol} N \} x = \\
& \quad \left\{ \frac{4}{(s-l)N} \operatorname{sol} \frac{4}{(s-l)N} - \frac{4}{SN-N+SN+N} + \frac{4}{(s+l)N} \operatorname{sol} \frac{4}{(s+l)N} - \right. \\
& \quad \left. \left[\frac{4}{(s-l)N} \right] \operatorname{sol} \frac{4}{(s-l)N} - \frac{4}{SN-N+SN+N} + \frac{4}{(s+l)N} \operatorname{sol} \frac{4}{(s+l)N} - N - \frac{2}{N} \operatorname{sol} N \right\} x = \\
& \quad \left\{ \frac{4}{(s-l)N} + \right. \\
& \quad \left[\frac{4}{(s-l)N} \right] \operatorname{sol} \frac{4}{(s-l)N} - \frac{4}{(s+l)N} + \frac{4}{(s+l)N} \operatorname{sol} \frac{4}{(s+l)N} - \frac{4}{(s-l)N} + \\
& \quad \left[\frac{4}{(s-l)N} \right] \operatorname{sol} \left\{ \frac{4}{SN-N+K2} \right\} - \frac{4}{(s+l)N} + \frac{4}{(s+l)N} \operatorname{sol} \frac{4}{(s+l)N} - N - \frac{2}{N} \operatorname{sol} N \} x = \\
& \quad \left\{ \frac{4}{(s+l)N} - \frac{2}{N} + \right.
\end{aligned}$$

Therefore,

$$\begin{aligned}
 \langle P_{A+-} \rangle &= \frac{-8(N_A + N_B)e^{-4J} + \sqrt{64(N_A + N_B)^2 e^{-8J} + 4 \times 64 e^{-4J}(1 - e^{-4J})(N_A + N_B)}}{2(1 - e^{-4J})} \\
 &= \frac{-4Ne^{-4J} + \{16N^2 e^{-8J} + 4 \times 16 e^{-4J}(1 - e^{-4J})\}^{1/2}}{2(1 - e^{-4J})} \\
 &= \frac{-4Ne^{-4J} + \sqrt{16N^2 e^{-8J} + 16N^2(1 - s^2)e^{-4J}(1 - e^{-4J})}}{2(1 - e^{-4J})} \\
 &= \frac{-4Ne^{-4J} + \sqrt{16N^2 e^{-8J} + 16N^2 e^{-8J}(1 - s^2)(e^{-4J} - 1)}}{2(1 - e^{-4J})} \\
 &= \frac{-4Ne^{-4J} + 4Ne^{-4J}[1 + (1 - s^2)(e^{-4J} - 1)]^{1/2}}{2(1 - e^{-4J})} \\
 &= 2N \frac{[1 + (1 - s^2)(e^{-4J} - 1)]^{1/2} - 1}{e^{-4J} - 1}
 \end{aligned}$$

(8.28)*

(8.29)*

Following exactly the same procedure, we obtain

$$\langle P_{B+-} \rangle = 2N \frac{[1 + (1 - s^2)(e^{-4J} - 1)]^{1/2} - 1}{e^{-4J} - 1}$$

(8.29)*

(8.30)*

From equation (8.17),

$$\frac{\langle Q_{++} \rangle \langle Q_{--} \rangle}{\langle Q_{+-} \rangle \langle Q_{-+} \rangle} = e^{-4J'}$$

$$\langle Q_{++} \rangle \langle Q_{--} \rangle e^{4J'} = \langle Q_{+-} \rangle \langle Q_{-+} \rangle$$

Now applying the relations (8.20) and (8.22),

$$\begin{aligned}
 (8N_{A+-} \langle Q_{+-} \rangle) (8N_{B+-} \langle Q_{+-} \rangle) e^{4J'} &= \langle Q_{+-} \rangle (8N_{A--} - \langle Q_{--} \rangle) \\
 &= \langle Q_{+-} \rangle (8N_{A--} - 8N_{B--} + \langle Q_{--} \rangle)
 \end{aligned}$$

Rearranging the terms,

$$\begin{aligned}
 & [64(N_A N_{B-}) - 8(N_{A+} + N_{B-}) \langle Q_{+-} \rangle + \langle Q_{+-} \rangle^2] e^{4J'} = 8(N_{A-} - N_{B-}) \langle Q_{+-} \rangle + \langle Q_{+-} \rangle^2 \\
 & \langle Q_{+-} \rangle^2 (e^{4J'} - 1) - [8(N_{A+} + N_{B-}) e^{4J'} + 8(N_{A-} - N_{B-})] \langle Q_{+-} \rangle + 64N_{A+} N_{B-} e^{4J'} = 0 \\
 & \langle Q_{+-} \rangle^2 (e^{4J'} - 1) - [8 \frac{N(1+s)}{N(1+s) - N(1-s)} e^{4J'} + 8 \frac{N(1-s)}{N(1+s) - N(1-s)}] \langle Q_{+-} \rangle \\
 & \quad + 64 \frac{N^2(1+s)(1-s)}{16} e^{4J'} = 0 \\
 & \langle Q_{+-} \rangle^2 (e^{4J'} - 1) - [2(2N + N(s-s')) e^{4J'} + 2(-N(s-s'))] \langle Q_{+-} \rangle + 4N^2(1+s)(1-s') e^{4J'} = 0 \\
 & \langle Q_{+-} \rangle^2 (e^{4J'} - 1) - 2N[2 + s - s'] e^{4J'} - (s-s') \langle Q_{+-} \rangle + 4N^2(1+s)(1-s') e^{4J'} = 0 \\
 & \langle Q_{+-} \rangle^2 (e^{4J'} - 1) - 2N[2e^{4J'} + (s-s') (e^{4J'} - 1)] \langle Q_{+-} \rangle + 4N^2(1+s)(1-s') e^{4J'} = 0 \\
 & \langle Q_{+-} \rangle^2 (e^{4J'} - 1) - 2N[(2 + s - s') (e^{4J'} - 1) + 2] \langle Q_{+-} \rangle + 4N^2(1+s)(1-s') e^{4J'} = 0 \\
 & \langle Q_{+-} \rangle \\
 & = \frac{2N[(2 + s - s') (e^{4J'} - 1) + 2] - \sqrt{4N^2[(2 + s - s') (e^{4J'} - 1) + s]^2 - 16N^2(1+s)(1-s') e^{4J'} (e^{4J'} - 1)}}{2(e^{4J'} - 1)} \\
 & = N \left\{ (2 + s - s') + \frac{2}{e^{4J'} - 1} \right\} - N \left\{ (2 + s - s') + \frac{1}{e^{4J'} - 1} \right\}^2 - \frac{4e^{4J'}}{e^{4J'} - 1} (1 + s)(1 - s')^{\frac{1}{2}} \} (8.30)^* \\
 & \quad (8.33)^*
 \end{aligned}$$

In equation (8.32), the first, the sixth, and the seventh integrations are easily obtained by inspection. Therefore, detailed integrations will be carried out only for the remaining integrals.

Second term:

Let

$$1 + (1 - s^2)e^{4C/kT} - 1 = t^2$$

$$(1 - s^2)e^{4C/kT} \left(-\frac{4C}{k}\right) \frac{dT}{T^2} = 2t \, dt$$

$$(1 - s^2)e^{4C/kT} \left(-\frac{2C}{k}\right) \frac{dT}{T^2} = t \, dt$$

$$e^{4C/kT} = \frac{(t + s)(t - s)}{1 - s^2}$$

$$\frac{dT}{T^2} = -\frac{k}{2C} \cdot \frac{t \, dt}{(1 - s^2)e^{4C/kT}} = -\frac{k}{2C} \cdot \frac{t(1 - s^2) \, dt}{(1 - s^2)(t + s)(t - s)}$$

$$= -\frac{k}{2C} \frac{t \, dt}{(t + s)(t - s)}$$

Therefore,

$$\begin{aligned} \int \frac{[1 + (1 - s^2)e^{4C/kT} - 1]}{(e^{4C/kT} - 1) T^2} \, dT &= \int -\frac{k}{2C} \frac{t^2 - 1}{(t + s)(t - s)} \, dt \\ &= -\frac{k}{2C} \int \frac{(1 - s^2)(t - 1)t \, dt}{(t + 1)(t - 1)(t + s)(t - s)} = -\frac{k}{2C} \int \frac{(1 - s^2)t \, dt}{(t + 1)(t + s)(t - s)} \end{aligned}$$

In order to integrate by parts, coefficients, A, B, and D are found as follows:

$$\frac{t}{(t + 1)(t + s)(t - s)} = \frac{A}{t + 1} + \frac{B}{t + s} + \frac{D}{t - s}$$

where

$$A = \frac{1}{(1 + s)(s - 1)}, \quad B = \frac{1}{2(1 - s)} \quad \text{and} \quad D = \frac{1}{2(1 + s)}$$

Therefore,

$$\begin{aligned}
 & -\frac{k}{2C} \int \frac{(1-s^2)t \, dT}{(t+s)(t-s)} \\
 & = -\frac{k}{2C}(1-s^2) \int \left[\frac{1}{(1+s)(s-1)(t+1)} + \frac{1}{2(1-s)(t+s)} + \frac{1}{2(1+s)(t-s)} \right] dT \\
 & = -\frac{k}{2C} \int \left[-\frac{1}{t+1} + \frac{1+s}{2(t+s)} + \frac{1-s}{2(t-s)} \right] dT \\
 & = -\frac{k}{4C} \int \left[-\frac{1}{2} + \frac{1}{t+s} + \frac{1}{1+s} + \frac{1}{1-s} - \frac{s}{1-s} \right] dT \\
 & = -\frac{k}{4C} \left\{ -2 \log \left(\frac{t+1}{2} \right) + (1+s) \log \left(\frac{t+s}{1+s} \right) + (1-s) \log \left(\frac{t-s}{1-s} \right) \right\}
 \end{aligned}$$

Third term:

Similarly, by letting $t'^2 = 1 + (1-s'^2)(e^{4C/kT} - 1)$,

$$\begin{aligned}
 & \left[\frac{1 + (1-s'^2)(e^{4C/kT} - 1)}{(e^{4C/kT} - 1)^2} \right] \frac{1}{T^2} dT \\
 & = -\frac{k}{4C} \left\{ -\log \left(\frac{t'+1}{2} \right) + (1+s') \log \left(\frac{t'+s'}{1+s'} \right) + (1-s') \log \left(\frac{t'-s'}{1-s'} \right) \right\}
 \end{aligned}$$

Fourth term:

$$\begin{aligned}
 & \left\{ 2 + s - s' + \frac{2}{e^{4C'/kT} - 1} \right\} \frac{dT}{T^2} = \int (s - s') \frac{dT}{T^2} + \frac{2(e^{4C'/kT} - 1) + 2}{e^{4C'/kT} - 1} \frac{dT}{T^2} \\
 & \int (s - s') \frac{dT}{T^2} = -\frac{(s - s')}{T} \\
 & \int \frac{2(e^{4C'/kT} - 1) + 2}{e^{4C'/kT} - 1} \frac{dT}{T^2} = \int \frac{2e^{4C'/kT} - 2 + 2}{e^{4C'/kT} - 1} \frac{dT}{T^2}
 \end{aligned}$$

$$= \int \frac{2}{1 - e^{-\mu_C'/kT}} \frac{dT}{T^2}$$

Let

$$m = 1 - e^{-\mu_C'/kT}$$

$$dm = \frac{\mu_C'}{k} e^{-\mu_C'/kT} \frac{dT}{T^2}$$

$$\frac{dT}{T^2} = \frac{k}{\mu_C'} \frac{dm}{e^{-\mu_C'/kT}} = \frac{k}{\mu_C'} \frac{dm}{(1-m)}$$

$$\int \frac{2(e^{\mu_C'/kT} - 1)}{1 - e^{-\mu_C'/kT}} + 2 \frac{dT}{T^2} = \int \frac{2e^{\mu_C'/kT}}{1 - e^{-\mu_C'/kT}} \frac{dT}{T^2}$$

$$= \int \frac{2}{m} \left(\frac{k}{\mu_C'} \right) \frac{dm}{1-m} = \frac{2k}{\mu_C'} \int \left(\frac{1}{m} + \frac{1}{1-m} \right) dm$$

$$= \frac{k}{2C'} [\log m - \log(1-m)]$$

$$= \frac{k}{2C'} \log \frac{m}{1-m}$$

$$\int \left[2 + s - s' + \frac{2}{e^{\mu_C'/kT} - 1} \right] \frac{dT}{T^2} = - \frac{s - s'}{T} + \frac{k}{2C'} \log \frac{m}{1-m}$$

Fifth term:

$$\int \left\{ \left[2 + s - s' + \frac{2}{e^{\mu_C'/kT} - 1} \right]^2 - \frac{4e^{\mu_C'/kT}}{e^{\mu_C'/kT} - 1} (1+s)(1-s') \right\}^{1/2} \frac{dT}{T^2}$$

$$\int \left\{ \left[\left(2 + s - s' + \frac{2}{e^{\mu_C'/kT} - 1} \right)^2 - \frac{4(1+s)(1-s')}{1 - e^{-\mu_C'/kT}} \right]^{1/2} \right\} \frac{dT}{T^2}$$

$$\begin{aligned}
&= \int \left\{ \left[\frac{(2 + s - s') e^{\mu_C' / kT} - (s - s')}{e^{\mu_C' / kT} - 1} \right]^2 - \frac{\mu_C' / kT}{1 - e^{-\mu_C' / kT}} \right\}^{1/2} \frac{dT}{T^2} \\
&= \int \left\{ \left[\frac{2e^{\mu_C' / kT} + (s - s')(e^{\mu_C' / kT} - 1)}{e^{\mu_C' / kT} - 1} \right]^2 - \frac{\mu_C' / kT}{1 - e^{-\mu_C' / kT}} \right\}^{1/2} \frac{dT}{T^2} \\
&= \int \left\{ \left[\frac{1 - e^{-\mu_C' / kT}}{1 - e^{-\mu_C' / kT}} + (s - s') \right]^2 - \frac{\mu_C' / kT}{1 - e^{-\mu_C' / kT}} \right\}^{1/2} \frac{dT}{T^2} \\
&= \int \left\{ (s - s')^2 + \frac{\mu_C' / kT}{1 - e^{-\mu_C' / kT}} + \frac{\mu_C' / kT}{1 - e^{-\mu_C' / kT}} + \frac{\mu_C' / kT}{(1 - e^{-\mu_C' / kT})^2} \right\}^{1/2} \frac{dT}{T^2} \\
&= \int \left\{ (s - s')^2 - \frac{\mu_C' / kT}{1 - e^{-\mu_C' / kT}} + \frac{\mu_C' / kT}{(1 - e^{-\mu_C' / kT})^2} \right\}^{1/2} \frac{dT}{T^2}
\end{aligned}$$

Now let

$$m = 1 - e^{-\mu_C' / kT}$$

$$dm = -\frac{\mu_C' / kT}{1 - e^{-\mu_C' / kT}} \frac{dT}{T^2}$$

$$\frac{dT}{T^2} = -\frac{k}{\mu_C'} \frac{dm}{(1 - m)}$$

Substituting these notations, we obtain

$$\begin{aligned}
&\int \left\{ (2 + s - s') + \frac{\mu_C' / kT}{e^{\mu_C' / kT} - 1} \right\}^2 - \frac{\mu_C' / kT}{e^{\mu_C' / kT} - 1} \right\}^{1/2} \frac{dT}{T^2} \\
&= \frac{k}{\mu_C'} \int \frac{2}{m(1 - m)} \left[\left(\frac{s - s'}{4} \right)^2 - (1 - ss')m + 1 \right]^{1/2} dm \\
&= -\frac{k}{2\mu_C'} \left\{ \int \frac{1}{m} \left(\frac{s - s'}{4} \right)^2 m^2 - (1 - ss')m + 1 \right\}^{1/2} dm + \int \frac{1}{1 - m} \left[\left(\frac{s - s'}{4} \right)^2 m^2 - (1 - ss')m + 1 \right]^{1/2} dm
\end{aligned}$$

For convenience, let

$$M = \frac{(s-s')^2}{4} - (1-ss')m + 1$$

and

$$a = \frac{(s-s')^2}{4}, \quad b = -(1-ss'), \quad c = 1$$

Then, the first term in the above equation becomes

$$\begin{aligned} \int \frac{\sqrt{M}}{m} dm &= \sqrt{M} + \frac{b}{2} \left(\frac{dm}{\sqrt{M}} + C \right) \frac{dm}{m \sqrt{M}} \\ &= \sqrt{M} + \frac{b}{2} \left[\frac{1}{\sqrt{a}} \log(2am + b + 2\sqrt{a}\sqrt{M}) + C \left[-\frac{1}{\sqrt{C}} \log \left(\frac{\sqrt{M} + \sqrt{C}}{m} + \frac{b}{2\sqrt{C}} \right) \right] \right] \\ &= \sqrt{M} - \frac{(1-ss')}{2} \left\{ \frac{2}{s-s'} \log \left[\frac{(s-s')^2}{2} m - (1-ss') + 2 \frac{(s-s')}{2} \sqrt{M} \right] \right. \\ &\quad \left. - \log \left[\frac{\sqrt{M} + 1}{m} - \frac{1-ss'}{2} \right] \right\} \\ &= \sqrt{M} - \frac{1-ss'}{s-s'} \log \left[(s-s') \sqrt{M} - (1-ss') + \frac{(s-s')^2}{2} m \right] \\ &\quad - \log \left[2 \frac{\sqrt{M} + 2 - (1-ss')m}{2m} \right] \\ &= \sqrt{M} - \frac{1-ss'}{s-s'} \log \left[(s-s') \sqrt{M} - (1-ss') + \frac{(s-s')^2}{2} m \right] \\ &\quad - \log \frac{\sqrt{M} - \frac{1-ss'}{2} m + 1}{m} \end{aligned}$$

For the second term, let

$$M = \frac{(s-s')^2}{4} m^2 - (1-ss')m + 1$$

$$a = 1, b = -(1 - ss'), c = \frac{(s - s')^2}{4}$$

$$q = (s^2 - 1)(1 - s'^2)$$

$$v = a' + b'm = 1 - m, a' = 1, b' = -1$$

$$\beta = bb' - 2a'c = (1 - ss') - \frac{(s - s')^2}{2}$$

$$k = ab'^2 - a'bb' + ca'^2 = 1 - (1 - ss') + \frac{(s - s')^2}{4} = \frac{(s + s')^2}{4}$$

$$\begin{aligned} & \int \frac{1}{1-m} \left[\frac{(s-s')^2}{4} m^2 - (1-ss')m + 1 \right]^{1/2} dm = \int \frac{\sqrt{M}}{v} dm \\ &= -\frac{1}{b'^2} (-b'\sqrt{M} - k \int \frac{dm}{v\sqrt{M}} - \frac{1}{2}\rho \int \frac{dm}{\sqrt{M}}) \\ &= -\left\{ -b'\sqrt{M} - k \left[\frac{1}{\sqrt{k}} \log \frac{2k + \rho\sqrt{v} - 2b'\sqrt{kM}}{v} - \frac{1}{2}\rho \frac{1}{\sqrt{v}} \log \left[\left(\frac{2cm+b}{4} \right) + \sqrt{\left(\frac{2cm+b}{4} \right)^2 + 1} \right] \right] \right\} \\ &= -\sqrt{M} + \frac{(s+s')^2}{4} \log \frac{(s+s')^2}{(s+s')} - \frac{1-m}{2} \log \left\{ \frac{(s+s')^2}{2(1-ss')} - \frac{(s-s')^2}{2} \right\} (1-m) + 2 \frac{s+s'}{2} \frac{\sqrt{M}}{2} \\ &+ \frac{1}{2} \frac{2(1-ss')}{2} \frac{(s-s')^2}{2} \log \left\{ \frac{(s-s')^2}{(s-s')} \frac{m}{(s^2-1)(1-s'^2)} - \frac{(s-s')^2}{4} m = (1-ss') \right\} \\ &+ \left[\left(\frac{(s-s')^2}{(s^2-1)(1-s'^2)} \right)^2 + 1 \right]^{1/2} \} \\ &= -\sqrt{M} + \frac{s+s'}{2} \log \frac{(s+s')\sqrt{M}}{(1-ss')} + \frac{[(1-ss') - \frac{(s-s')^2}{2}](1-m) + \frac{(s+s')^2}{2}}{1-m} \end{aligned}$$

$$\begin{aligned}
& + \left(\frac{1-s-s'}{s-s'} - \frac{(s-s')}{2} \right) \log \left\{ \frac{\frac{(s-s')^2}{2} - m - (1-s-s')}{\sqrt{(s^2-1)(1-s'^2)}} + \left[\frac{\frac{(s-s')^2}{2} - m - (1-s-s')}{(s^2-1)(1-s'^2)} \right]^{1/2} \right\} \\
& = -\sqrt{m} + s + s' \log \frac{(s+s')\sqrt{m} + \left[\frac{(1-s-s')}{2} - \frac{(s-s')^2}{2} \right] (1-m) + \frac{(s+s')^2}{2}}{1-m} \\
& + \left[\frac{(1-s-s')}{s-s'} - \frac{(s-s')}{2} \right] \log \left\{ (s-s')\sqrt{m} - (1-s-s') + \frac{(s-s')^2}{2} m \right\}
\end{aligned}$$

Now combining both terms and rearranging,

$$\begin{aligned}
& \int \left(\frac{\sqrt{m}}{m} + \frac{\sqrt{m}}{1-m} \right) dm \\
& = \sqrt{m} - \frac{1-s-s'}{s-s'} \log \left[(s-s')\sqrt{m} - (1-s-s') + \frac{(s-s')^2}{2} m \right] - \log \left[\frac{\sqrt{m} - \frac{1-s-s'}{2} m + 1}{m} \right] \\
& - \sqrt{m} + \left[\frac{1-s-s'}{s-s'} - \frac{s-s'}{2} \right] \log \left[(s-s')\sqrt{m} - (1-s-s') + \frac{(s-s')^2}{2} m \right] \\
& + \frac{s+s'}{2} \log \left\{ \frac{(s+s')\sqrt{m} + \left[\frac{(1-s-s')}{2} - \frac{(s-s')^2}{2} \right] (1-m) + \frac{(s+s')^2}{2}}{1-m} \right\} \\
& = -\frac{s-s'}{2} \log \frac{\sqrt{m} + \frac{s-s'}{2} m - \frac{1-s-s'}{2}}{1/(s-s')} - \log \frac{\sqrt{m} - \frac{1-s-s'}{2} m + 1}{m} \\
& + \frac{s+s'}{2} \log \frac{(s+s')\sqrt{m} - [(1-s-s') - \frac{(s-s')^2}{2}] m + \frac{2-2ss' - s^2 - s'^2 + 2ss' + s^2 + 2ss' + s'^2}{2}}{1-m} \\
& = -\frac{s-s'}{2} \log \frac{\sqrt{m} + \frac{s-s'}{2} m - \frac{1-s-s'}{2}}{1/(s-s')} - \log \frac{\sqrt{m} - \frac{1-s-s'}{2} m + 1}{m}
\end{aligned}$$

$$\begin{aligned}
& + \frac{s+s'}{2} \log \left\{ \frac{\sqrt{N} - \left[\frac{1-ss'}{s+s'} - 2 \frac{(s-s')^2}{s+s'} \right] m + \frac{1+ss'}{s+s'}}{1/(s+s')(1-m)} \right\} \\
& = - \frac{(s-s')}{2} \log \left[\frac{\sqrt{N} + \frac{s-s'}{2} m - \frac{1-ss'}{s-s'}}{1/(s-s')} \right] - \log \left[\frac{\sqrt{N} - \frac{1-ss'}{2} m + 1}{m} \right] \\
& + \frac{s+s'}{2} \log \left[\frac{\sqrt{N} - \frac{2-2ss'-s^2}{2(s+s')} - \frac{2+2ss'}{1/(s+s')(1-m)} + \frac{1+ss'}{s+s'}}{1/(s+s')(1-m)} \right] \\
& = - \frac{(s-s')}{2} \log \left[\frac{\sqrt{N} + \frac{s-s'}{2} m - \frac{1-ss'}{s-s'}}{1/(s-s')} \right] - \log \left[\frac{\sqrt{N} - \frac{1-ss'}{2} m + 1}{m} \right] \\
& + \frac{s+s'}{2} \log \left[\frac{\sqrt{N} + \left(\frac{s+s'}{2} - \frac{1+ss'}{s+s'} \right) m + \frac{1+ss'}{s+s'}}{1/(s+s')(1-m)} \right] \\
& \int \left[\left(2 + s - s' + \frac{2}{e^{4C'/kT} - 1} \right)^2 - \frac{4C'/kT}{e^{4C'/kT} - 1} (1+s)(1-s') \right]^{1/2} \frac{dT}{T^2} \\
& = - \frac{k}{2C'} \left\{ - \frac{(s-s')}{2} \log \left[\frac{\sqrt{N} + \frac{s-s'}{2} m - \frac{1-ss'}{1/(s-s')}}{s-s'} \right] - \log \left[\frac{\sqrt{N} - \frac{1-ss'}{2} m + 1}{m} \right] \right. \\
& \quad \left. + \frac{s+s'}{2} \log \left[\frac{\sqrt{N} + \left(\frac{s+s'}{2} - \frac{1+ss'}{s+s'} \right) m + \frac{1+ss'}{s+s'}}{1/(s+s')(1-m)} \right] \right\}
\end{aligned}$$

Substituting all these integrals into equation (8.32), we finally obtain:

$$\begin{aligned}
& - \int \frac{\langle W \rangle}{T^2} dT \\
& = -AN(C-C') \frac{1}{T} + \frac{4CNk}{4C} \left\{ -2 \log \left(\frac{t+1}{2} \right) + (1+s) \log \frac{t+s}{1+s} + (1-s) \log \frac{t-s}{1-s} \right.
\end{aligned}$$

$$\begin{aligned}
& -2 \log \left(\frac{t' + 1}{2} \right) + (1 + s') \log \left(\frac{t' + s'}{1 + s'} \right) + (1 - s') \log \left(\frac{t' - s'}{1 - s'} \right) \\
& + 4C'N \left[-\frac{(s - s')}{T} + \frac{k}{2C'} \log \frac{m}{1 - m} \right] + 4C'N \frac{k}{2C'} \left\{ -\frac{(s - s')}{2} \log \left[\frac{\sqrt{m} + \frac{s - s' - m - \frac{1 - ss'}{s - s'}}}{1/(s - s')} \right] \right. \\
& \left. - \log \left[\frac{\sqrt{m} - \frac{1 - ss'}{2} m + 1}{1 - m} \right] + \frac{s + s'}{2} \log \left[\frac{\sqrt{m} + \frac{s + s' - 1 + ss'}{2} m + \frac{1 + ss'}{s + s'}}{1/(s + s')(1 - m)} \right] \right\} \\
& + 4C'N \frac{(s - s')}{T} - \frac{N \mu_0 H}{2} \frac{(s + s')}{T} \\
& = -4N(C - C')/T + kN \left\{ -2 \log \frac{t + 1}{2} + (1 + s) \log \frac{t + s}{1 + s} + (1 - s) \log \frac{t - s}{1 - s} \right. \\
& - 2 \log \frac{t' + 1}{2} + (1 + s') \log \frac{t' + s'}{1 + s'} + (1 - s') \log \frac{t' - s'}{1 - s'} \left. \right\} \\
& + 2kN \left\{ -\frac{(s - s')}{2} \log \frac{\sqrt{m} + \frac{s - s' - m - \frac{1 - ss'}{s - s'}}}{1/(s - s')} - \log \frac{\sqrt{m} - \frac{1 - ss'}{2} m + 1}{1 - m} \right. \\
& \left. + \frac{s + s'}{2} \log \frac{\sqrt{m} + \left(\frac{s + s' - 1 + ss'}{2} m + \frac{1 + ss'}{s + s'} \right)}{1/(s + s')(1 - m)} \right\} \\
& - \frac{N \mu_0 H}{2T} (s + s')
\end{aligned}$$

(8.33)*

(8.36)*

In the expansion of equation (8.35), the result obtained by Yomosa⁵ was used.

(8.37)*

Applying the conditions $\frac{\partial F}{\partial s} = 0$ and $\frac{\partial F}{\partial s'} = 0$, we obtain the following equations:

$$\begin{aligned}
\frac{\partial F}{\partial s} = & -\frac{N}{2} \mu_0 H - \frac{3}{4} NkT \left\{ (1+s) \frac{\partial}{\partial s} \log (1+s) + \log (1+s) \frac{\partial}{\partial s} (1+s) \right. \\
& + (1-s) \frac{\partial}{\partial s} \log (1-s) + \log (1-s) \frac{\partial}{\partial s} (1-s) \left. \right\} + NkT \left\{ (1+s) \frac{\partial}{\partial s} \log (t+s) \right. \\
& + \log (t+s) \frac{\partial}{\partial s} (1+s) + (1-s) \frac{\partial}{\partial s} (t-s) + \log (t-s) \frac{\partial}{\partial s} (1-s) - 2 \frac{\partial}{\partial s} \log (t+1) \left. \right\} \\
& + NkT \left\{ s'm + \frac{m^2}{2} \left[s' + \frac{2s(1-s'^2)}{4} \right] + \dots \right\}
\end{aligned}$$

Here t = constant when $s = 0$ in $t^2 = 1 + (1-s^2)(e^{4C/kT} - 1)$

$$\begin{aligned}
\frac{\partial F}{\partial s} = & -\frac{N}{2} \mu_0 H - \frac{3}{4} NkT \{ 1 + \log (1+s) - 1 - \log (1-s) \} + NkT \{ 1 + \log (t+s) \\
& \sim 1 - \log (t-s) \} + NkT \left\{ \frac{s}{4} m^2 + \frac{m}{2} (m+s)s' - \frac{ss'^2}{4} m^2 \right\} = 0
\end{aligned}$$

Dividing through by $\frac{NkT}{2}$,

$$-\frac{\mu_0 H}{kT} - \frac{3}{2} \log \left(\frac{1+s}{1-s} \right) + 2 \log \left(\frac{t+s}{t-s} \right) + \frac{m^2}{2} + m(m+2)s' - \frac{ss'^2}{2} m^2 = 0$$

similarly,

$$\begin{aligned}
\frac{\partial F}{\partial s} = & -\frac{\mu_0 H}{kT} - \frac{3}{2} \log \left(\frac{1+s'}{1-s'} \right) + 2 \log \left(\frac{t'+s'}{t'-s'} \right) + \frac{1}{2} m^2 s' + m(m+2)s - \frac{m^2}{2} s'^2 = 0 \quad (8.37)^* \\
& (8.39)^*
\end{aligned}$$

From equation (8.37)*

$$\left(\frac{\partial^2 F}{\partial s \partial s'} \right) = m(m+2) - \frac{s'^2}{2} m^2$$

By the condition $s = s' = 0$,

$$\left(\frac{\partial^2 F}{\partial s \partial s'}\right)^2 = [m(m+2)]^2$$

Again, from equation (8.27),

$$\begin{aligned}\frac{\partial^2 F}{\partial s^2} &= -\frac{3}{2} \frac{\partial}{\partial s} \log \frac{1+s}{1-s} + 2 \frac{\partial}{\partial s} \log \frac{t+s}{t-s} + \frac{m^2}{2} - \frac{s'^2}{2} m^2 \\ &= -\frac{3}{2} \left(\frac{1-s}{1+s} \right) \frac{\partial}{\partial s} \left(\frac{1+s}{1-s} \right) + 2 \left(\frac{t-s}{t+s} \right) \frac{\partial}{\partial s} \left(\frac{t+s}{t-s} \right) + \frac{m^2}{2} - \frac{s'^2}{2} m^2 \\ &= -\frac{3}{2} \left(\frac{1-s}{1+s} \right) \frac{(1-s) + (1+s)}{(1-s)^2} + 2 \left(\frac{t-s}{t+s} \right) \frac{(t-s) + (t+s)}{(t-s)^2} + \frac{m^2}{2} - \frac{s'^2}{2} m^2 \\ &= -\frac{3}{2} \frac{(1-s) + (1+s)}{(1+s)(1-s)} + 2 \frac{(t-s) + (t+s)}{(t+s)(t-s)} + \frac{m^2}{2} - \frac{s'^2}{2} m^2\end{aligned}$$

Now, putting the condition $s = s' = 0$,

$$\frac{\partial^2 F}{\partial s^2} = -\frac{3}{2} \frac{2}{2} + \frac{2}{t^2} 2t + \frac{m^2}{2} = -3 + 4t^{-1} + \frac{m^2}{2}$$

similarly,

$$\frac{\partial^2 F}{\partial s'^2} = -3 + 4t^{-1} + \frac{m^2}{2}$$

$$\left(\frac{\partial^2 F}{\partial s \partial s'}\right)^2 - \left(\frac{\partial^2 F}{\partial s^2}\right) \left(\frac{\partial^2 F}{\partial s'^2}\right) = [m(m+2)]^2 - \left[\frac{m^2}{2} + 4t^{-1} - 3\right]^2 = 0$$

$$m(m+2) - \frac{m^2}{2} - 4t^{-1} + 3 = 0$$

or

$$m^2 - \frac{m^2}{2} + 2m - 4t^{-1} + 3 = 0$$

Since m is very small, neglecting m^2 terms,

$$2m - 4t - 1 + 3 = 0$$

substituting the equilibrium value of m and t , i.e.,

$$m = 1 - e^{-4C/kT}, \text{ and } t^2 = 1 + (1 - s^2)(e^{4C/kT} - 1),$$

we obtain

$$2 = 2e^{-4C/kT} - 4e^{-2C/kT} + 3 = 0$$

or

$$4e^{-2C/kT} + 2e^{-4C/kT} - 5 = 0$$

$$(8.39)^*$$

BIOGRAPHICAL SKETCH

Samuel Sang Myung Kim was born in Pyung-Yang, Korea, on October 10, 1928. He attended Chosun Christian University, majoring in chemistry; he received the degree of Bachelor of Science in 1951. His undergraduate training was interrupted for one year when he was called into military service on the outbreak of the Korean conflicts.

In 1955, he entered the Graduate School of the University of Florida. He has since that time held the Naval Stores Research Fellowship.

He is a member of the professional chemical fraternity, Alpha Chi Sigma.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February, 1962.


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